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THE UNIVERSITY OF ALBERTA

EFFECT OF SOLVENT AND TEMPERATURE  
ON DIFFUSION COEFFICIENTS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
IN PARTIAL FULFILMENT OF THE REQUIREMENTS OF THE DEGREE  
OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

BY

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UNIVERSITY OF ALBERTA  
FACULTY OF GRADUATE STUDIES

The undersigned hereby certify that they have read,  
and recommend to the Faculty of Graduate Studies for acceptance,  
a thesis entitled

EFFECT OF SOLVENT AND TEMPERATURE  
ON DIFFUSION COEFFICIENTS

submitted by John E. Evanoff, B. Sc. in partial fulfilment of  
the requirements for the degree of Master of Science in  
Chemistry.





ABSTRACT

The effect of solvent and temperature on the diffusion coefficients of some organic nitro compounds was investigated using polarographic and viscosity measurements. The viscosity for the glycerol and ethylene glycol systems varied between about 130 poise and 0.02 poise for the temperature range 0° to 100°C, i.e. representing a variation of a factor of about 6000. The diffusion coefficients obtained from polarographic measurements and the Ilkovic Equation and from viscosity measurements and the Stokes-Einstein Equation are of similar magnitude.

An attempt was made to correlate the diffusion coefficients obtained from viscosity data with those obtained from polarographic data. The results indicate that the viscosity is not the only factor affecting the diffusion coefficients. The nature of the solvent is a minor factor also affecting diffusion coefficients.







### ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

A	cross-sectional area
C	concentration, millimoles/liter; viscometer constant
D	diffusion coefficient, $\text{cm}^2/\text{sec}$
d	density, g/ml
g	acceleration due to gravity
$F_t$	pycnometer constant at temperature $t^\circ\text{C}$
$I_d$	diffusion current constant, $i_d/\text{Cm}^{2/3}t^{1/6}$
k	Boltzmann's constant, $1.38 \times 10^{-16}$ ergs/degree
M	molar concentration; molecular weight
m	rate of flow of mercury, mg/sec
N	Avogadro's number
n	number of faradays per mole of electrode reaction
R	gas constant
r	radius, cm
s	quantity of solute
T	temperature, $^\circ\text{K}$ or $^\circ\text{C}$
t	time, seconds
V	molar volume
W	weight, g
x	distance
$\delta$	mobility
$\eta$	viscosity, poise
$1/\eta$	fluidity, $\text{poise}^{-1}$



## I INTRODUCTION

The interest in the diffusion of small molecules in viscous solvents is due to the rapid advance in the last decade of the use of gas chromatography as a method of analysis. Diffusion rates are important in gas chromatography because of their effect on plate height and column efficiency. The general relation for the variation of plate height with carrier-gas flow rate is usually associated with van Deemter, Zuiderweg and Klinkenberg (43). This relation attributes band broadening at high flow rates mainly to a resistance to mass transfer in the liquid phase. In other words the slow rate of mass transfer from the liquid to the moving gas phase, and vice versa, is caused by a low rate of diffusion of solute molecules in the liquid phase. Hence a knowledge of diffusion coefficients in viscous liquids would allow one to gain further understanding of the effects of resistance to mass transfer.

At present, few measurements of diffusion coefficients in viscous liquids have been made and the methods employed for determining diffusion coefficients in any liquid are usually laborious.

### General Methods for Diffusion Coefficient Measurements

The general methods for determining diffusion coefficients are normally based on either of Fick's two laws





(38a)

of diffusion. Fick's first law, which describes the process of translational diffusion in one direction is given as (27)

$$\frac{\partial s}{\partial t} = - D A \frac{\partial C}{\partial x} \quad \dots 1$$

where  $\partial s$  is defined as the quantity of solute diffusing across a boundary of cross-sectional area  $A$  in the time  $\partial t$ ;  $\partial C / \partial x$  is the concentration gradient where  $C$  is concentration and  $x$  is distance and  $D$  is a proportionality factor defined as the diffusion coefficient. Fick's second law is a more general relationship and is given as (50)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \dots 2$$

Equation 2 is based on the assumption that the diffusion coefficient is independent of concentration. Providing Equation 2 can be integrated, the diffusion coefficient can be determined from measurements of either  $\partial C / \partial x$  or concentration as a function of distance and time.

It would not be feasible, in this dissertation, to discuss in detail all of the various methods available for the determination of the diffusion coefficient. The processes that may be involved in these methods may be classified as free, restricted and steady-state diffusion. These three general processes are briefly described below. For those readers interested in a more thorough discussion of the methods available for determining diffusion coefficients, review articles by Weissberger (49), Neurath (36) and Harned





(16) are recommended.

The experimental methods employing free diffusion, which are based on Fick's second law, involve the formation of an initially sharp boundary between the two phases, with the more dense phase on the bottom of a diffusion cell. The diffusion cell itself should be tall enough so that the composition at the bottom and at the top of the cell remains unchanged during the period of observation. The most generally applicable methods of determining the concentration or concentration gradient in the diffusion cell are optical which involve determining the refractive-index gradient that is established. The refractive index gradient is related to the concentration gradient and hence to the diffusion coefficient. Two of the most common methods applied to the case of free diffusion are the Lamm Scale Method (a refractometric method) (51) and the Schlieren Method (a refractometric scanning method) (52).

In restricted diffusion we have a continuation of the process of free diffusion wherein concentration changes are measured at the ends of the column or diffusion cell. Measurements are made during the latter stages of the process, i.e. when the concentration difference between the two ends of the cell approaches zero. Two of the common methods used for the restricted diffusion process are the method of Layer Analysis (53) in which discrete layers of the diffusion



column are sampled and analyzed and the Electrical Conductance Method (54) which is limited to electrolytes.

In steady-state diffusion the first law of Fick serves as a means of computing the diffusion coefficient. Diffusion takes place through a region in which the concentration gradient is independent of time. An example of this method is the porous-plate method of Northrup and Anson (55). This method requires a calibration with some substance of known diffusivity in the same solvent so the diffusion coefficient obtained is a relative one.

In this investigation, diffusion coefficients are obtained from polarographic measurements and the Ilkovic Equation. This could be classified as a steady-state method and is one of the simplest techniques for diffusion coefficient measurement and furthermore it is applicable to dilute solutions. Since the measurement of diffusion coefficients by any method, including the polarographic one, requires a great deal of experimental finesse, it would be convenient to establish a generalized relation between the diffusion coefficient and some more simply measureable property such as viscosity. One could then simply determine the viscosity and calculate the diffusion coefficient. This type of calculation should be possible by means of the Stokes-Einstein Equation if the correct values of the constants are obtained from measurements of diffusion coefficients in viscous





solvents. In this research an attempt has been made to correlate diffusion coefficients obtained from polarographic measurements with viscosity, to allow one to calculate diffusion coefficients of other systems merely from viscosity measurements.

### Diffusion Coefficients and the Ilkovic Equation

The Ilkovic Equation is derived in part from a form of Fick's first law, i.e. the fundamental differential equation for symmetrical spherical diffusion, given as (24).

$$\frac{\partial c}{\partial t} = D \left[ \frac{\partial^2 c}{\partial x^2} - \frac{2}{x} \left( \frac{\partial c}{\partial x} \right) \right] \quad \dots 3$$

Derivation of the Ilkovic Equation, relating diffusion current to concentration of the diffusing species, is performed by applying Equation 3 to the case of an expanding spherical electrode, the dropping mercury electrode (25).

For the purposes of this research, the Ilkovic Equation was used in the form (26)

$$i_d = 607nD^{1/2} C m^{2/3} t^{1/6} \quad \dots 4$$

where  $i_d$  is the average diffusion current in microamperes,  $n$  the number of faradays per mole of electrode reaction,  $D$  the diffusion coefficient in  $\text{cm}^2/\text{second}$ ,  $C$  the concentration of diffusing species in millimoles/liter,  $m$  the rate of flow of mercury in  $\text{mg}/\text{second}$ ,  $t$  the drop time in seconds





and  $m^{2/3}t^{1/6}$  the capillary constant in  $mg^{2/3} \text{ seconds}^{-1/2}$ . Equation 4 predicts a linear relationship between diffusion current and concentration. There is ample evidence to support this experimentally with a variety of compounds in a variety of solvents: metal ions have been studied in aqueous solutions and also in nonaqueous solvents such as ethylenediamine (39), acetonitrile (22,23), ethylene glycol (5,12) and alcohols ranging from methanol to pentanol (5). The same linearity was found for nitroparaffins (9,18,35,40) and substituted nitrobenzenes (7,37) in aqueous solutions, acid halides in acetone (1), organic halogen compounds in dimethylformamide (30), nitrobenzene and some of its derivatives in glycerol (8), dimethylformamide (21), acetonitrile (13,14), aqueous dioxane (11), ethanol/benzene mixtures (15) and nitroparaffins in a variety of nonaqueous solvents ranging from methanol to glycerol (38).

Change of solvent from aqueous solution can affect the diffusion current in several ways. First, a change in the surface tension of the mercury causing a change in the drop time, hence a change in the capillary constant. The constancy of the capillary constant in varying solvent media is shown by the data of Walter and Rosalie (45) for water/dioxane mixtures in which they reported a variation of  $\pm 1.6$  percent in the capillary constant. Similarly, the data of DeVries and Bruss (8) for glycerol solutions in which a



variation of  $\pm 1.1$  percent is noted. However, in this study, any variation in the capillary constant is accounted for since the value of this term was determined for each run. Second, the solvent may change the diffusion current because of its effect on the diffusion coefficient. Because of increased viscosity it is usually smaller in nonaqueous solvent.

Lingane and Kolthoff (34) experimentally verified the correctness of the numerical constant 607 of Equation 4 and the diffusion coefficient term for a number of metal ions in 0.1M potassium chloride solutions. These workers give evidence that the observed diffusion coefficient obtained by polarography agree with those obtained from equivalent conductance measurements. Their results for thallous, lead iodate and chromate ions show an agreement of about  $\pm 2$  percent between observed and calculated diffusion coefficients. We therefore assume that the determination of diffusion coefficients from the Ilkovic Equation is justified.

Nitro compounds were chosen in this study because their polarographic behaviour is fairly well known. The current-voltage curves one obtains are well defined and therefore allow for easy analysis.

#### Diffusion Coefficients and the Stokes-Einstein Equation

An expression which describes the effect of solvent viscosity on the diffusion coefficient is the Stokes-Einstein





Equation (29)

$$D = \frac{kT}{6\pi\eta r} \quad \dots 5$$

where  $k$  is Boltzmann's constant,  $1.38 \times 10^{-16}$  ergs/degree,  $T$  the absolute temperature,  $\eta$  the viscosity and  $r$  the radius of the diffusing species. Equation 5 relates the diffusion coefficient of a particle,  $D$ , to the viscosity of the solvent medium. It is obtained from Equation 6, relating the diffusion coefficient of a particle to its mobility,  $\delta$  (27), and Stokes law (41) (Equation 7)

$$D = kT\delta \quad \dots 6$$

$$\text{where} \quad \delta = \frac{1}{6\pi\eta r} \quad \dots 7.$$

Stokes law relates the mobility of large spherical particles, i.e. particles larger than the molecules of the solvent, to the viscosity of the medium.

As pointed out in the preceeding paragraph, the Stokes-Einstein Equation is applicable to the special case where the diffusing particles are larger than those of the solvent medium. The choice of the factor  $6\pi$  is based on the assumption that the medium can be regarded as homogeneous and there is no slippage between the solvent and diffusing molecules. For the case when the diffusing particles are equal to or slightly larger than the solvent molecules the factor  $6\pi$  in Equation 5 is replaced by the





factor  $4\pi$  (32). This factor is chosen to account for slippage between the diffusing particles and the solvent molecules. The expression for the diffusion coefficient under these conditions then becomes (32)

$$D = \frac{kT}{4\pi\eta r} \quad \dots 8$$

Equation 8 includes the case of self-diffusion.

To apply Equation 8 to the determination of diffusion coefficients it is necessary to know the radius of the particles in question. If we are dealing with spherical molecules which are not solvated, we can express the radius in terms of the molar volume of the substance. The molar volume,  $V$ , is defined as

$$V = M/d \quad \dots 9$$

where  $M$  is the molecular weight and  $d$  is the density of the substance in the pure state. If we write

$$2r = (V/N)^{1/3} \quad \dots 10$$

where  $N$  is Avogadro's number, Equation 8 can be written as

$$D = \frac{k}{2\pi} \left( \frac{N}{V} \right)^{1/3} \frac{T}{\eta} \quad \dots 11$$

Equation 11 predicts that the diffusion coefficient is a linear function of the viscosity-temperature ratio when applied to the case of self-diffusion. In other words the



product of the diffusion coefficient and the viscosity-temperature ratio should be a constant:

$$D \frac{\eta}{T} = \text{a constant} \quad \dots 12$$

The constancy of this product, to within 3 percent, was observed by Wang and coworkers (46-48) for the self-diffusion of water between 0° and 55°C.

Li and Chang (32) report fair agreement between Equation 11 and experimental data. They found that the value of the function  $(kT/D\eta) (N/V)^{1/3}$  varied between 5.4 and 8.3 when applied to experimental data. This range of values compares favorably with the value predicted by Equation 11, i.e.  $2\pi$  (6.28). As stated previously, Equation 11 is applicable to the case where the diffusing species are of the same size as the solvent molecules. In general, when one applies this equation to the case of small diffusing species, i.e. small with respect to the solvent molecules, it is necessary to adjust the factor  $2\pi$  to take into account the size of the diffusing species. The diffusion of small molecules in solvents consisting of large molecules has not been investigated to any extent. Lamm's (31) study of the diffusion of water in glycerol seems to indicate that the factor in Equation 11 should be replaced by a smaller factor. Since the condition of interest in gas chromatography is the case of small solute molecules diffusing in a solvent consisting





of large molecules it would be convenient to have an equation of the form of Equation 11. Such an equation should apply with the appropriate alteration in the factor  $2\pi$ , i.e.

$$D = \frac{k}{a\pi} \left(\frac{N}{V}\right)^{1/3} \frac{T}{\eta} \quad \dots 13$$

where "a" is a coefficient characteristic of small solute molecules diffusing in a solvent consisting of large molecules.





## II EXPERIMENTAL

### Reagents

Fisher reagent grade ethylene glycol and glycerol were used without further purification as solvents. Fisher reagent grade lithium chloride was dried for 24 hours at <sup>an</sup> 100°C and stored in a dessicator before use as/indifferent electrolyte. Eastman reagent grade nitroethane, 1- and 2-nitropropane, nitrobenzene, o-nitrotoluene, 2-nitro-p-xylene, 3-nitro-o-xylene and K and K\* reagent grade 1- and 2-nitrobutane were used without further purification. Stock solutions of 0.1M LiCl in ethylene glycol and glycerol were prepared and stored under a nitrogen atmosphere.

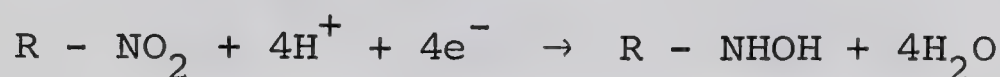
The solutions for polarographic measurements were preferably prepared by weighing. A concentrated solution, ca. 0.1M with respect to the reducible compound, was first prepared by adding a sufficient amount of the reducible compound to the stock 0.1M LiCl solution above. A portion of this concentrated solution was then diluted in a 100 ml volumetric flask with the 0.1M LiCl-ethylene glycol or 0.1M LiCl-glycerol to give the desired concentration of about  $10^{-3}$  M. 100 ml of final solution was sufficient for the solvent saturator and measurements of the diffusion current, capillary constant and viscosity. All dilutions were carried out at 25°C.

\*K & K Laboratories, Plainview, New York.



Polarography of Organic Nitro Compounds in Ethylene Glycol  
and Glycerol

It is generally accepted that the reduction of organic nitro compounds proceeds through a 4 electron step to form the corresponding hydroxylamine (7,9,18,21,35,37,38, 40), i.e.



Radin and DeVries (38) used the diffusion coefficient reported for nitromethane in methanol (19) along with diffusion currents obtained for nitromethane in methanol and calculated a value of 3.9 (i.e. 4) for the number of electrons,  $n$ , from the Ilkovic Equation. They observed wave heights and half-wave potentials of the same order of magnitude for several other nitroparaffins. They concluded it was logical to assume the same value for  $n$  for all nitroparaffins. Similarly, Pearson (37) obtained  $n = 3.92$  (i.e. 4) for nitrobenzene in aqueous solutions from calculations involving the Ilkovic Equation and the diffusion coefficient of the benzoate ion from conductivity data (28). Therefore on the basis of the above evidence it will be assumed that a value of  $n$  equal to 4 is justified in this research.

The current-voltage curves obtained for the nitro compounds were well formed and symmetrical in both ethylene glycol and glycerol (Figures 1 and 2). However, due to the





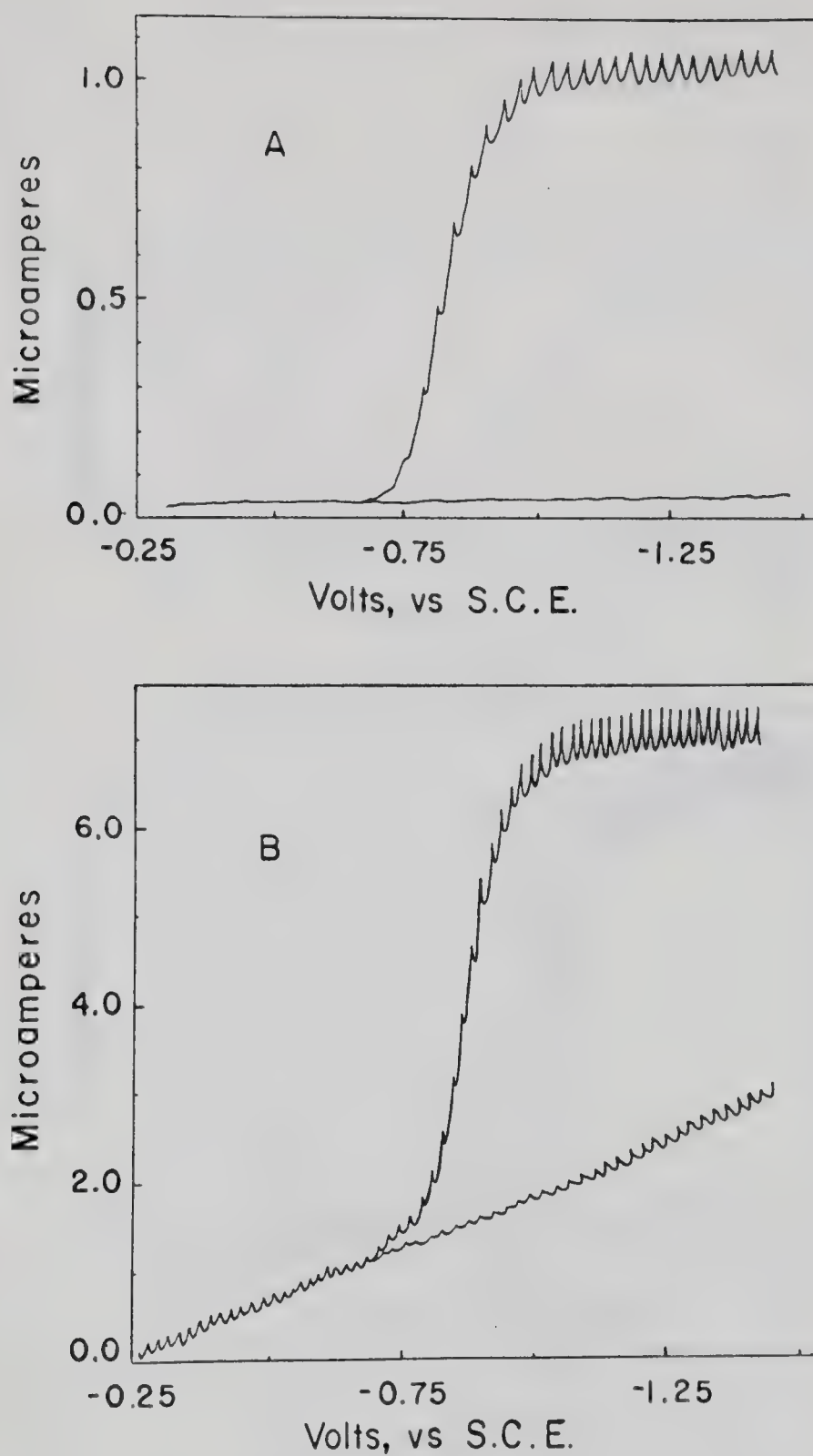


Figure 1. Polarograms of  $5.3 \times 10^{-4}$  M nitrobenzene in 0.1M LiCl-ethylene glycol (0.005 percent in gelatin) using a Ag/AgCl reference electrode. A, 0°C; B, 100°C. The bottom line is the residual current.



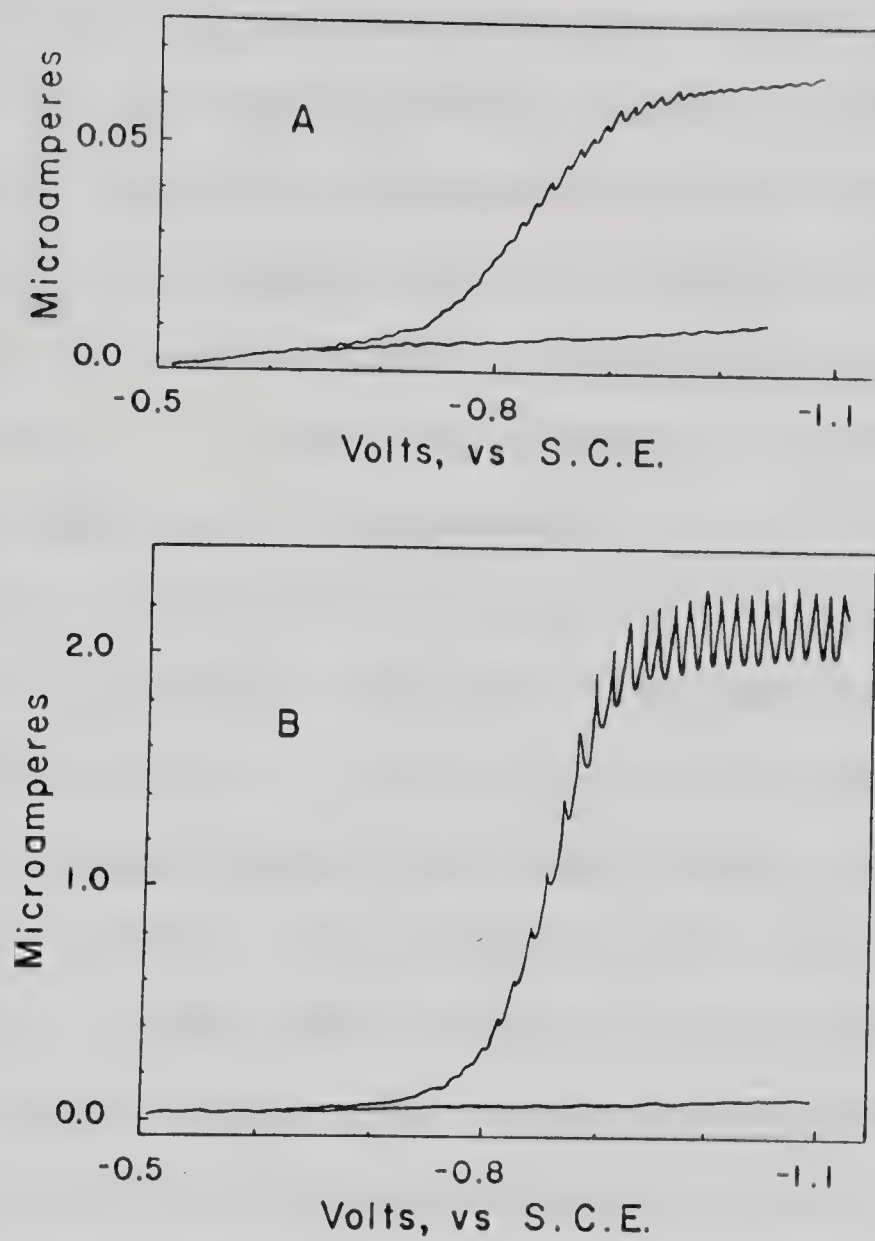


Figure 2. Polarograms of  $5.5 \times 10^{-4}$  M nitrobenzene in 0.1M LiCl-glycerol using a Ag/AgCl reference electrode. A, 0°C; B, 100°C. The bottom line is the residual current.





viscous nature of the two solvents employed a number of difficulties were encountered. Deaeration with purified nitrogen (Linde) took more time than for aqueous solutions. It was necessary to purge the solutions with nitrogen for approximately 30 minutes to ensure complete removal of oxygen from the 0.1M LiCl-ethylene glycol and the 0.1M LiCl-glycerol solutions. Deaeration of the ethylene glycol-based solutions was carried out at 0°C. Glycerol-based solutions were so viscous at 0°C that they needed to be deaerated at a higher temperature and 25°C was used.

After deaeration it was noticed that solutions of glycerol were milky due to the many fine bubbles of nitrogen trapped in the solution. Since the solutions were viscous at the deaeration temperature these fine bubbles would move slowly to the surface. The solutions were stored up to twelve hours in a dessicator under a nitrogen atmosphere to allow them to clear before measurements were made. Current-voltage curves on solutions stored in the above manner for as long as 24 hours showed no uptake of oxygen and therefore this procedure was followed for all the measurements. Preliminary measurements were also carried out on the above deaerated solutions to determine if a nitrogen atmosphere was necessary while the measurements were being made. A 0.1M LiCl solution was deaerated, allowed to clear and diffusion current measurements carried out after storage. After



removal from the dessicator the solution was examined immediately and again six hours later. No oxygen uptake was evident as the current-voltage curves in Figure 3 show. In all cases the dropping mercury electrode was immersed to a depth of at least 2.5 cm. To help prevent the loss of sample during deaeration, the nitrogen was presaturated with the solution being deaerated before passing into the electrolysis cell.

Since deaeration was carried out at 25°C for the glycerol-based solutions a preliminary check was carried out to see if the deaeration resulted in a sample loss. A solution, approximately  $10^{-3}$ M, of 2-nitropropane in 0.1M LiCl-glycerol was deaerated for 30 minutes at 25°C, allowed to clear and the polarogram recorded at 25°C. After an additional 20 minutes deaeration and subsequent storage to allow the solution to clear, another polarogram was obtained. No significant loss in sample was evident as revealed by the diffusion currents obtained: 0.312 microamperes after 30 minutes deaeration and 0.310 microamperes after an additional 20 minutes deaeration. Therefore it was assumed that no sample loss resulted and deaeration of the glycerol-based solutions was carried out at 25°C.

Due to the small diffusion currents (hence small diffusion coefficients) in the glycerol-based solutions, specifically at 0°C, it was thought that there might be a depletion of the reducible species in the vicinity of the





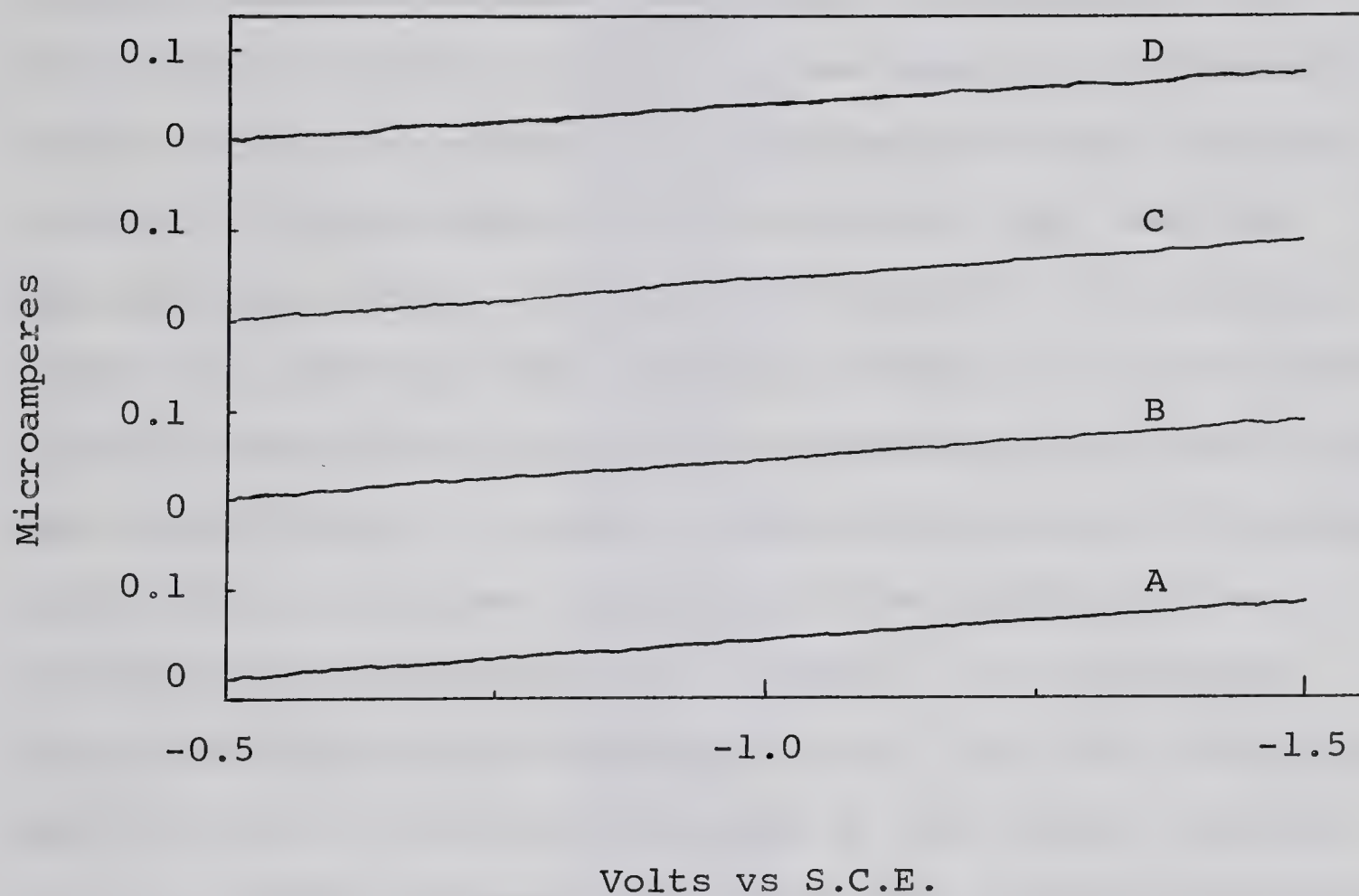


Figure 3. Residual current curves for 0.1M LiCl-glycerol at 25°C, using the same Compensation for Changing Current setting on the Metroholm Polarecord.

- A: after deaeration and 6 hour storage;
- B: A, 6 hours later;
- C: after deaeration and 24 hours storage;
- D: C, 6 hours later.



dropping mercury electrode. This would manifest itself in a decreasing diffusion current if the reduction was allowed to continue at a potential corresponding to some point on the diffusion current plateau. A solution, approximately  $10^{-3}\text{M}$  nitroethane in 0.1M LiCl-glycerol, was examined to determine if any significant change in the diffusion current plateau resulted. A polarogram at 0°C was obtained and then the potential was set at -1.6 volts (vs Ag/AgCl). This corresponded to a potential well along the diffusion current plateau. A short trace was obtained at this potential with the electrode then being allowed to remain at this potential for 10 minutes. Another short trace was obtained and the heights of the diffusion current plateaus were compared. No significant change was observed in the wave height: e.g. 24.5 mm initially and 24.2 after 10 minutes, a change of only about 1 percent.

Difficulty was encountered with erratic drop formation both at low and high temperatures. At low temperatures the drop, especially in the viscous glycerol-based solution, upon breaking from the capillary would not fall free of the electrode and often would merge with the next drop to form. This difficulty was overcome by grinding the electrode tip to a pencil point (42) and as evident from the photograph in Figure 4 the drops fall free of the electrode. No appreciable change in the value of the diffusion current was observed after grinding. For a  $1.5 \times 10^{-3}\text{M}$  solution of 1-nitropropane







Figure 4. Photograph of drop behaviour in 0.1M LiCl-glycerol. Temperature: 1°C; Viscosity: approximately 107 poise; drop time; 4.5 seconds. Photograph, actual size, single exposure, f5.4, 1/15 second.



in 0.1M LiCl-glycerol the diffusion current before grinding was 0.35 microamperes and after 0.344 microamperes. At higher temperatures, greater than 40°C, erratic drop formation appeared to result from wetting of the capillary due to the retreat of the mercury column up the capillary after a drop had broken free. This effect disappeared after the inside of the capillary was coated with silicone (20,44).

The temperature range studied was 0° to 100°C for the aromatic nitro compounds while the upper temperature was limited to 40° or 60°C for the nitroparaffins by virtue of their higher vapor pressures.

#### Polarographic Apparatus

The polarographic measurements were made with the aid of the Metrohm Polarecord E261, a recording polarograph. This polarograph was especially suited to low diffusion current measurement since it possessed high sensitivity ( $2.5 \times 10^{-8}$  amperes full scale deflection), a compensation for charging current and wide choice of voltage ranges.

The polarographic cell, illustrated in Figure 5, consisted of a silver/silver chloride reference electrode, the glass electrolysis cell, and a rubber stopper. The electrolysis cell was made from a 29 x 200 mm pyrex test tube shortened to 75 mm. The cell was fitted with a number 6 rubber stopper provided with two holes, one for the dropping





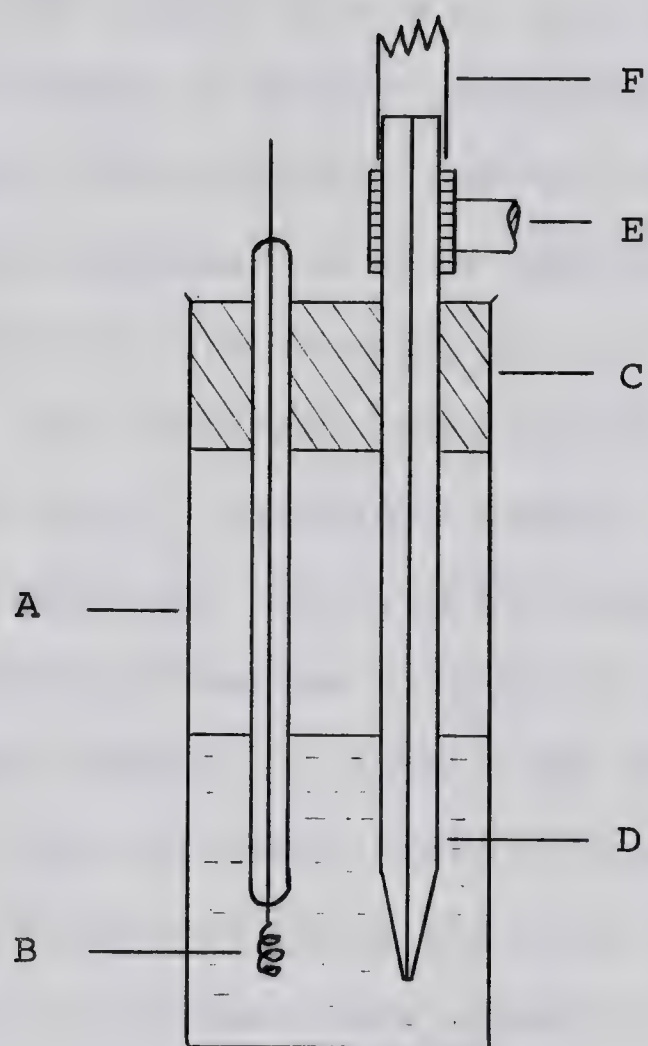


Figure 5. Electrolysis cell used for polarographic measurements. A, glass electrolysis cell; B, silver/silver chloride reference electrode; C, 2-hole rubber stopper; D, dropping mercury electrode; E, positioning clamp; F, Tygon tubing to mercury reservoir.



electrode and the other for the reference electrode. The silver/silver chloride reference electrode was prepared from 10 cm of 18 gauge silver wire (8). The silver wire was wound in a 4 mm spiral and sealed into 4 mm soft glass tubing. It was coated with a layer of silver chloride by making it the anode in a cell for approximately one-half hour at a constant current of 6.43 milliamperes in 0.1M hydrochloric acid. It was stored in 0.1M LiCl-ethylene glycol or 0.1M LiCl-glycerol when not in use. Two different dropping mercury electrodes were used in this study. Capillary number I was about 60 mm in length and was used for the 0.1M LiCl-ethylene glycol studies. This electrode became plugged so another was constructed, capillary number II, from a 100 mm length of marine barometer tubing (Corning Glass Works, Corning, N.Y.). The longer length was necessary since the bore of the capillary was larger. Both capillaries were ground to a pencil point and coated with Siliclad (Clay-Adams, Inc., New York), a water soluble silicone, for reasons stated previously. This coating involved drawing a one percent aqueous solution of Siliclad through the capillary for 5 minutes followed by rinsing with distilled water, drying for 24 hours at room temperature with a final drying for one-half hour at 100°C. During measurements the dropping mercury electrode was held vertically and at a reproducible height by a clamp situated above the electrolysis cell. This precaution was carried





out to minimize the variation in  $m^{2/3}t^{1/6}$  even though the value of this term was determined each time. The dropping mercury electrode was connected to the mercury reservoir with Tygon tubing.

The deaeration assembly, illustrated in Figure 6, consisted of a nitrogen source, a cooling coil, a solvent trap to saturate the gas with sample solution and a nitrogen bubbler. The cooling coil, B, was made from eight feet of 1/4 in. I.D. copper tubing wound in a three in. spiral. The solvent trap, C, was constructed from 19/38 ground glass joints and a coarse fritted glass gas dispersion tube. Two of these were constructed which allowed rapid interchange when a series of measurements were being carried out. The nitrogen bubbler, E, consisted of a short length of thermometer capillary (0.5 cm) sealed to a length of 4 mm soft glass tubing. This was mounted in a number 6 rubber stopper fitted with an exhaust tube. This type of bubbler produces small bubbles which bring about efficient deaeration.

A Dewar flask containing an ice/water mixture was used for thermostating at 0°C. Two Colara Ultra-Thermostat circulating baths, maintaining temperatures to  $\pm 0.05^\circ\text{C}$ , were used for temperatures 20° to 100°C. One bath was water filled for temperatures 20° to 50°C, the other was filled with industrial grade ethylene glycol for temperatures 50° to 100°C.



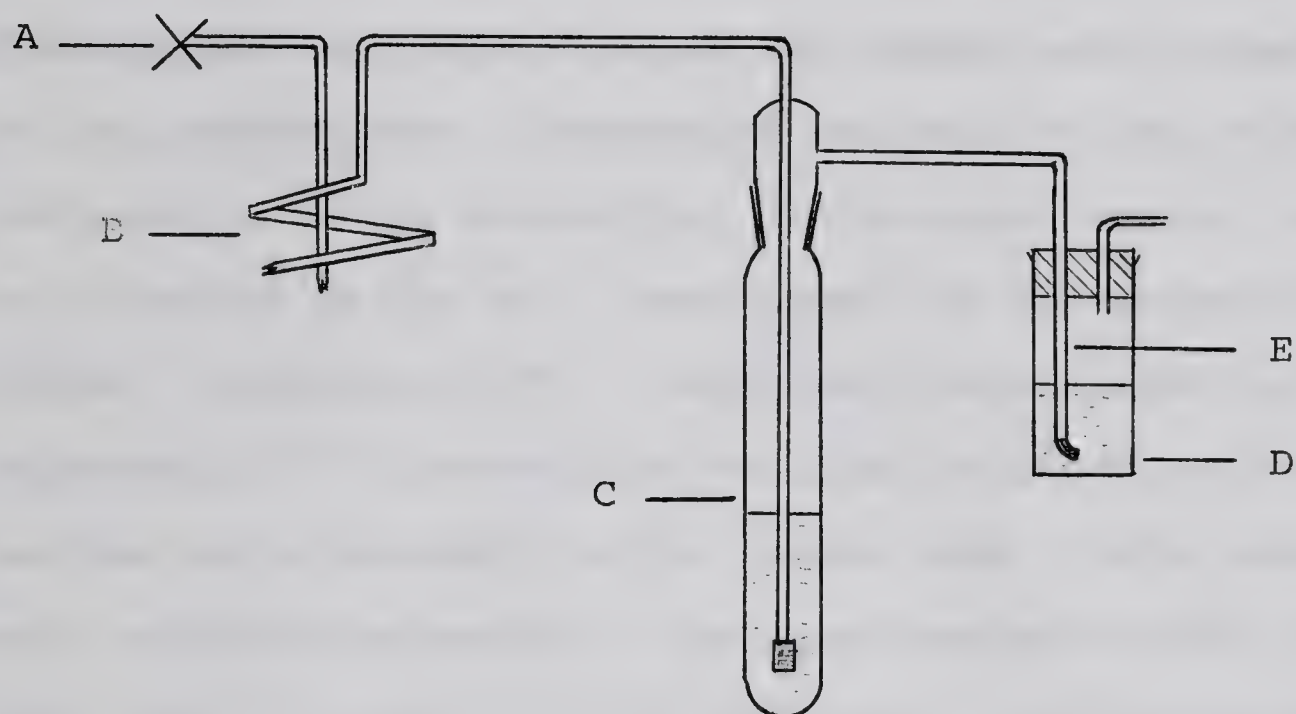


Figure 6. Deaeration assembly. A, nitrogen source; B, copper cooling coil; C, solvent saturator; D, glass electrolysis cell and sample solution; E, nitrogen bubbler.





### Diffusion Current Measurement

The sample solutions were made up in 100 ml volumetric flasks, containing 0.005 percent gelatin in those cases where preliminary investigation showed the need for maxima suppressors. A 15 ml aliquot was added to the electrolysis cell and 15 ml of the sample solution was placed in the presaturator. Deaeration was carried out as described previously. After deaeration, the dropping mercury electrode was inserted in the cell, positioned, and the polarogram recorded, initially at 0°C. Subsequent polarograms were recorded at 20° intervals on the same solution by transferring the whole assembly to the proper bath. Bath temperatures were regulated as needed. The time required to do a complete run, from 0° to 100°C at 20° intervals, took on the average four hours.

The height of the mercury column was about 37 cm. The values of  $m$  and  $t$  for each run were determined with the recording polarograph set at the observed half-wave potential by collecting and timing the flow of mercury through the capillary. This gave data for the calculation of the capillary constant for each run. The averages for the capillary constant, in both solvents, for temperatures ranging from 0° to 100°C are shown in Tables I and II. It is interesting to point out that the flow rate of mercury increases more with temperature when glycerol is used as



TABLE I. VALUES OF THE RATE OF FLOW OF MERCURY, DROP TIME AND THE CAPILLARY CONSTANT<sup>a</sup> IN 0.1M LiCl-ETHYLENE GLYCOL AS SOLVENT<sup>b</sup>

Temp., °C	Drop Time, t, seconds	Mass Flow Rate, m, mg sec <sup>-1</sup>	Capillary Constant, $m^{2/3}t^{1/6}$ , mg <sup>2/3</sup> sec <sup>-1/2</sup>	Standard Error of the Mean
0	4.66	1.29	1.53	0.01
20	4.28	1.33	1.54	0.01
40	3.77	1.36	1.53	0.02
60	3.40	1.34	1.50	0.02
80	3.08	1.38	1.50	0.02
100	3.02	1.38	1.50	0.02

a. Capillary I.

b. 0.005 percent in gelatin.





TABLE II. VALUES OF THE RATE OF FLOW OF MERCURY, DROP TIME AND THE CAPILLARY CONSTANT<sup>a</sup> IN 0.1M LiCl-GLYCEROL AS SOLVENT

Temp., °C	Drop Time, t, seconds	Mass Flow Rate, m, mg sec <sup>-1</sup>	Capillary Constant, $m^{2/3}t^{1/6}$ , mg <sup>2/3</sup> sec <sup>-1/2</sup>	Standard Error of the Mean
0	4.23	1.44	1.62	0.01
20	4.41	1.47	1.66	0.01
40	4.34	1.52	1.69	0.01
60	4.31	1.56	1.72	0.01
80	4.00	1.63	1.74	0.01
100	3.90	1.65	1.74	0.02

a. Capillary II.



solvent than when ethylene glycol is used. On the other hand the drop time decreases less.

Preliminary investigations as to the variation of diffusion current with concentration in both 0.1M LiCl-ethylene and 0.1M LiCl-glycerol were carried out. It was found that all the compounds tested showed the relation to be a linear one, which made it reasonable to use the diffusion current constant ( $I_d = i_d/Cm^{2/3}t^{1/6}$ ) (33) for calculating diffusion coefficients. Typical results are shown in Figures 7, 8 and 9, from the data in Tables III, IV and V for 1-nitropropane and nitrobenzene in 0.1M LiCl-ethylene glycol and in 0.1M LiCl-glycerol at 0°, 25°, 45°C and the range 0° to 100°C at 20° intervals.

#### Viscosity Measurement

Viscosities were determined on the same sample solutions that were examined polarographically. The measurements were obtained using calibrated Cannon-Fenske Routine Type Viscometers for transparent liquids. Choice of viscometer was dictated by the viscosity of the solution in question and / <sup>the viscometer was</sup> chosen such that the efflux time was between 200 and 600 seconds. A stopwatch, graduated in 0.2 second intervals, was used to determine efflux times. Viscometer constants at 37.78°C (100°F) and 98.89°C (210°F) were supplied with the viscometers. Values of the viscometer constant at





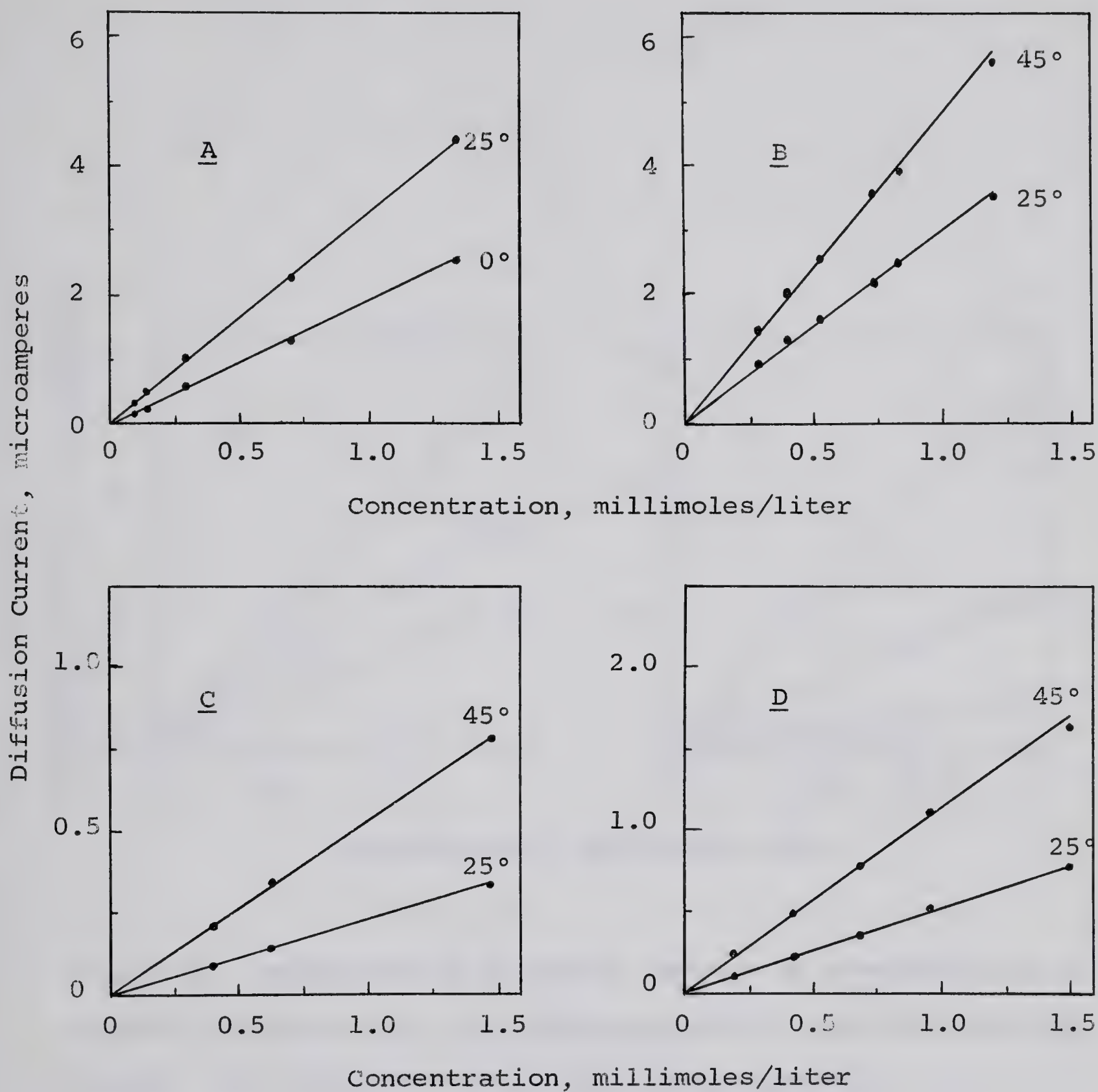


Figure 7. Dependence of diffusion current on concentration at various temperatures. A, B, l-nitropropane and nitrobenzene in 0.1M LiCl-ethylene glycol; C, D, l-nitropropane and nitrobenzene in 0.1M LiCl-glycerol.



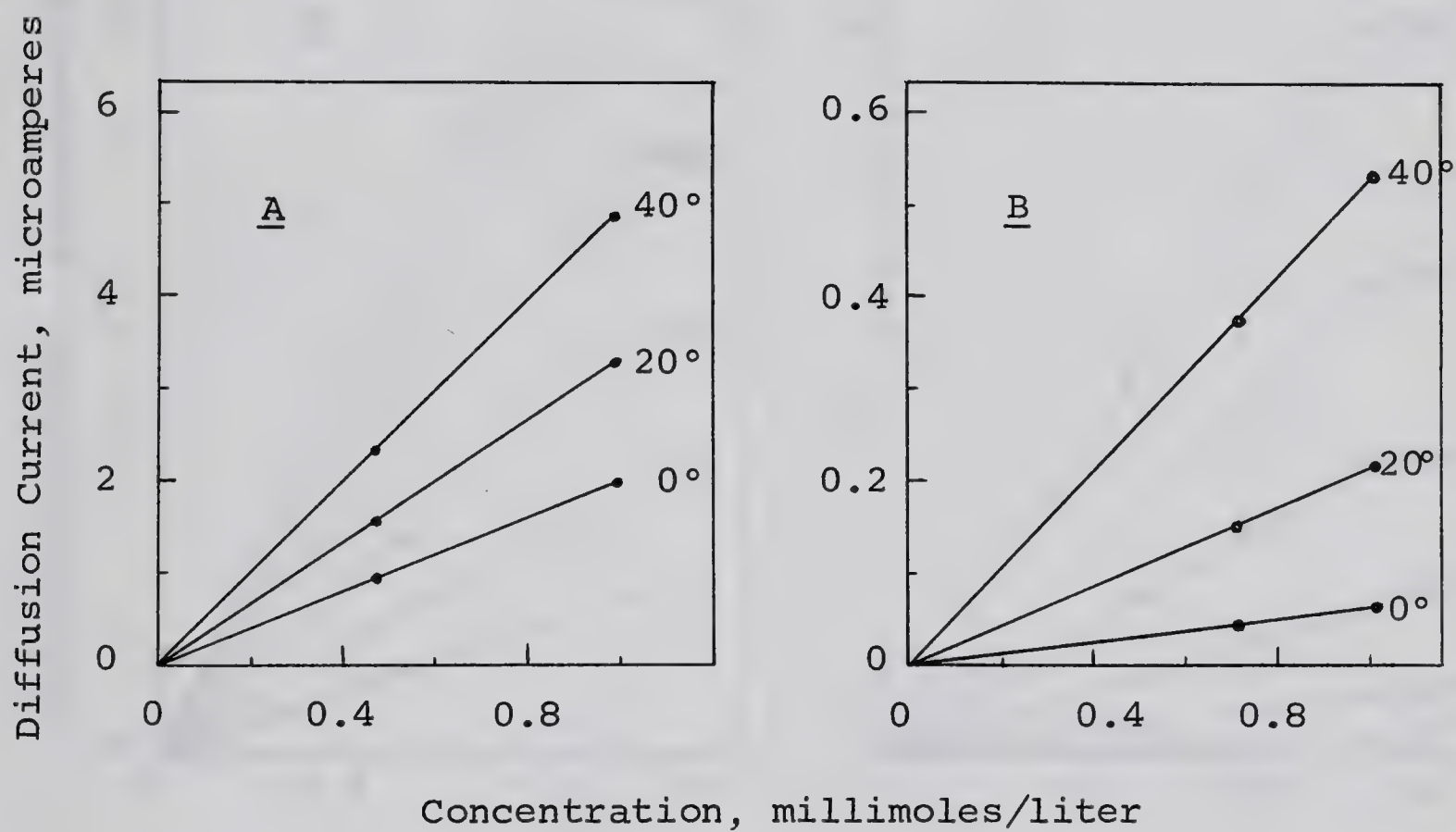


Figure 8. Dependence of diffusion current on concentration at various temperatures. A, 1-nitropropane in 0.1M LiCl-ethylene glycol; B, 1-nitropropane in 0.1M LiCl-glycerol.





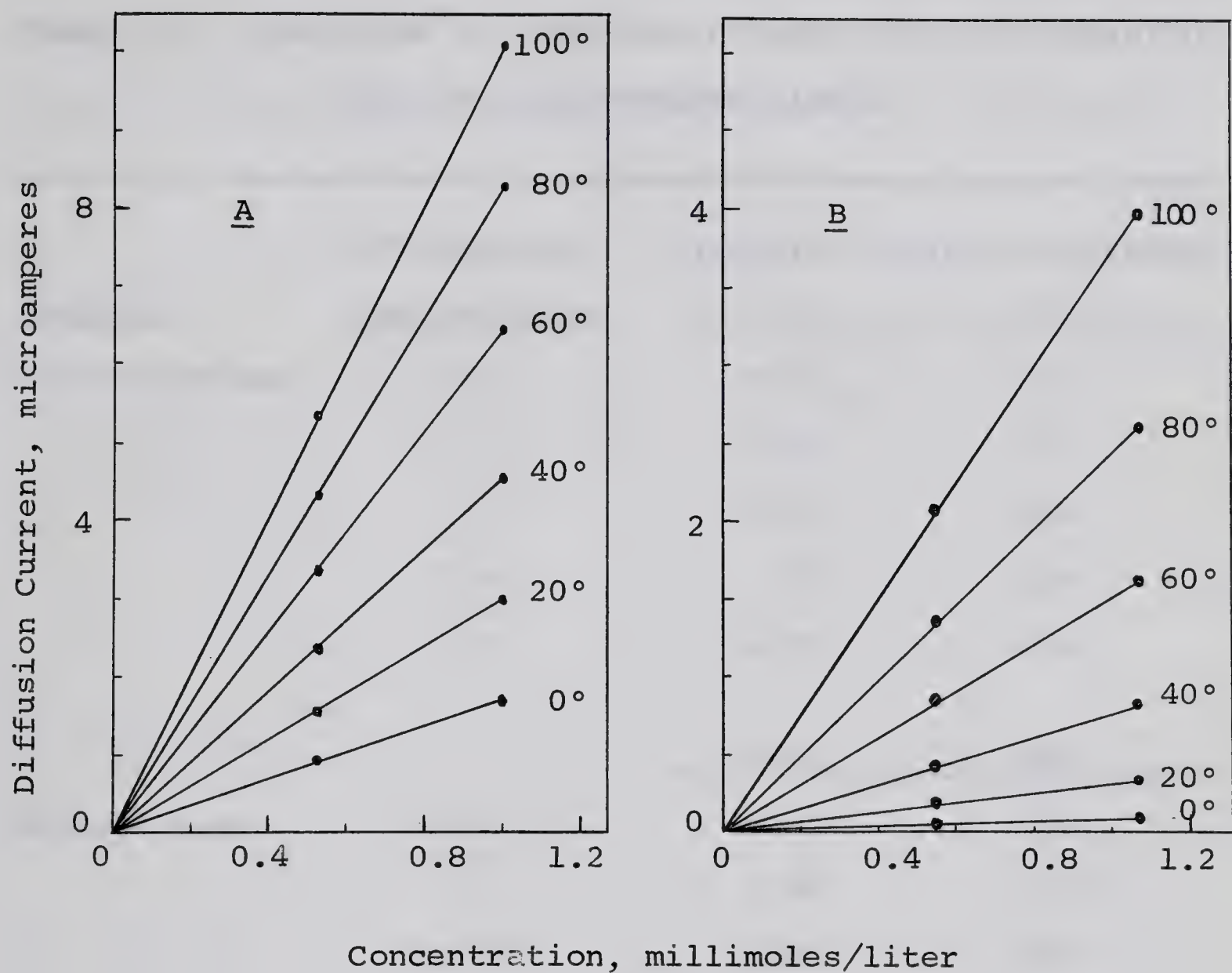


Figure 9. Dependence of diffusion current on concentration at various temperatures. A, nitrobenzene in 0.1M LiCl-ethylene glycol; B, nitrobenzene in 0.1M LiCl-glycerol.



TABLE III. VARIATION OF DIFFUSION CURRENT WITH CONCENTRATION  
IN 0.1M LiCl-ETHYLENE GLYCOL<sup>a</sup>

<u>Compound</u>	<u>Millimolar Concentration</u>	<u>Diffusion Current, microamp.</u>	
		<u>0°C</u>	<u>25°C</u>
1-Nitropropane	0.11	0.20 <sub>4</sub>	0.35
	0.14	0.33	0.50
	0.31	0.62	1.00
	0.69	1.35	2.22
	1.32	2.58	4.36
Nitrobenzene		<u>25°C</u>	<u>45°C</u>
	0.27	0.90	1.38
	0.41	1.36	2.13
	0.53	1.64	2.64
	0.74	2.24	3.58
	0.82	2.57	3.83
	1.20	3.61	5.65

a. 0.005 percent in gelatin.





TABLE IV. VARIATION OF DIFFUSION CURRENT WITH CONCENTRATION  
IN 0.1M LiCl-GLYCEROL

<u>Compound</u>	Millimolar <u>Concentration</u>	Diffusion Current, microamp.	
		<u>25°C</u>	<u>45°C</u>
1-Nitropropane	0.41	0.09	0.20
	0.66	0.15	0.34
	1.50	0.35	0.78
Nitrobenzene	0.21	0.10	0.25
	0.43	0.22	0.50
	0.68	0.35	0.78
	0.94	0.52	1.11
	1.50	0.79	1.63



TABLE V. VARIATION OF DIFFUSION CURRENT WITH TEMPERATURE AND CONCENTRATION IN 0.1M LiCl-ETHYLENE GLYCOL<sup>a</sup> AND 0.1M LiCl-GLYCEROL

<u>Compound</u>	<u>Millimolar Concentration</u>	<u>Diffusion Current, microamp.</u>					
		<u>0°</u>	<u>20°</u>	<u>40°</u>	<u>60°</u>	<u>80°</u>	<u>100°</u>
1-Nitropropane <sup>b</sup>	0.47	0.98	1.64	2.34			
	0.99	2.04	3.38	4.98			
1-Nitropropane <sup>c</sup>	0.72	0.05	0.16	0.39			
	1.01	0.07	0.22 <sub>5</sub>	0.54			
Nitrobenzene <sup>b</sup>	0.53	0.98	1.61	2.47	3.42	4.45	5.52
	1.00	1.82	3.10	4.73	6.60	8.40	10.2
Nitrobenzene <sup>c</sup>	0.55	0.05	0.17	0.42	0.83 <sub>5</sub>	1.35	2.08
	1.07	0.09 <sub>7</sub>	0.33 <sub>5</sub>	0.82	1.62	2.62	4.00

a. 0.005 percent in gelatin.

b. 0.1M LiCl-ethylene glycol.

c. 0.1M LiCl-glycerol.





temperatures other than these two were obtained by interpolation and extrapolation using the relation (2)

$$C_{T_x} = C_{T_1} - \frac{C_{T_1} - C_{T_2}}{T_1 - T_2} (T_1 - T_x) \quad \dots 14$$

where  $C_{T_x}$  is the viscometer constant at temperature  $T_x(^{\circ}\text{C})$ , and  $C_{T_1}$ ,  $C_{T_2}$  are the viscometer constants at temperatures  $T_1$  ( $37.78^{\circ}\text{C}$ ) and  $T_2$  ( $98.89^{\circ}\text{C}$ ), respectively. A correction for the difference in the acceleration due to gravity,  $g$ , at the calibration laboratory and at this laboratory was also carried out as follows

$$C_L = g_L / g_F \times C_F \quad \dots 15$$

where  $C_L$  and  $C_F$  are calibration constants and  $g_L$ ,  $g_F$  are the accelerations of gravity at the testing laboratory and calibrating laboratory, respectively. All viscometers used were corrected as outlined with calibration constants listed in Table VI.

Test temperatures for viscosity determinations were maintained with two Sargent circulating baths, Type NSI-12, one water filled for temperatures  $20^{\circ}$  and  $40^{\circ}\text{C}$ , the other filled with industrial grade ethylene glycol for temperatures  $60^{\circ}$ ,  $80^{\circ}$  and  $100^{\circ}\text{C}$ . Temperature control was  $\pm 0.01^{\circ}\text{C}$ . Thermostating at  $0^{\circ}\text{C}$  was carried out in an ice/water bath which consisted of a 6 x 11 in. Dewar flask strip



TABLE VI. VISCOMETER CONSTANTS

Viscometer		Viscometer Constant, centistokes/sec				
Number	0°	20°	40°	60°	80°	100° C
50V286	0.004024	0.004018	0.004012	0.004004	0.003998	0.003991
100H734	0.01563	0.01561	0.01538	0.01536	0.01534	0.01532
150E68	0.03667	0.03661	0.03655	0.03649	0.03643	0.03637
200D979	0.1052	0.1050	0.1049	0.1047	0.1045	0.1044
300C718	0.2551	0.2547	0.2542	0.2538	0.2534	0.2530
400J549	1.238	1.236	1.235	1.233	1.231	1.229
600V383	20.04	20.00	19.96	19.92	19.88	19.85





silvered leaving a 1 in. window for viewing. Temperature uniformity was obtained with an electric stirrer.

Viscometer holders were made from number 11 rubber stoppers by drilling two holes 13 mm and 8 mm in diameter with the center to center distance 25 mm. These were mounted on a Perspex bath cover in which were drilled 2 in. holes. Viscometer alignment was made visually with the aid of a plumb bob.

The kinematic viscosity was calculated from the efflux time,  $t$ , and the viscometer calibration constant:

$$\text{Kinematic viscosity, centistokes} = C_T \cdot t \quad \dots 16$$

The dynamic viscosity,  $\eta$ , was obtained from the relation

$$\eta = \text{kinematic viscosity} \times \text{density} \quad \dots 17$$

The viscometer was charged in the conventional manner with the sample solution that was being examined polarographically. After positioning in the proper bath, sufficient time was allowed for temperature equilibration. Five efflux time determinations were carried out on each solution and at each temperature. Time measurements were carried out to within 0.1 seconds with the stopwatch. Before another sample solution was examined the viscometer was cleaned by rinsing with distilled water, anhydrous methanol, followed by a final rinsing with petroleum ether. It was



dried with a stream of dried air. The viscometers were occasionally cleaned with chromic acid then rinsed and dried as stated previously.

### Density Measurement

Densities of the 0.1M LiCl-ethylene glycol and 0.1M LiCl-glycerol solutions and the pure nitro compounds were determined by the pycnometer technique. The pycnometers used were the Weld type of capacity 3 and 25 ml. The 3 ml pycnometer was used in determining the densities of the 1- and 2-nitrobutane since the amount available was small. Since a 3 ml pycnometer was not available one was constructed from a 2 ml volumetric flask to which was sealed the ground glass fitting from a conventional 25 ml pycnometer. Thermostating was carried out with the same constant temperature baths that were used for the viscosity determinations. Between determinations the pycnometers were cleaned with hot chromic acid, rinsed with distilled water, methanol, petroleum ether and vacuum dried. Two 25 ml and one 3 ml pycnometer were calibrated using freshly boiled distilled water. Calibrations were carried out at 20° intervals over the range 0° to 100°C. Duplicate determinations for the calibration factors were carried out at each temperature for each pycnometer with a variation no greater than  $\pm 2$  mg in the net weight of the water in the 25 ml pycnometer and no





greater than  $\pm 0.5$  mg in the net weight of the water in the 3 ml pycnometer. The pycnometer calibration factor,  $F_t$ , was obtained from

$$F_t = \frac{\text{density of water at } t^\circ\text{C } (d_t)}{\text{weight of water in the pycnometer at } t^\circ\text{C } (W_t)} \quad \dots 18$$

Density of water between  $0^\circ$  and  $100^\circ\text{C}$  were obtained from A.S.T.M. designation D-1480-57T. Calibration factors are listed in Table VII.

Duplicate determinations were carried out on each solution with the density, corrected to vacuum, calculated by the following equation:

$$\text{density in vacuum } (d_t), \text{ g/ml} = (F_t)(W_t) + C \quad \dots 19$$

where  $C$  is the vacuum correction obtained from

$$C = d_a [1 - (F_t W_t)] \quad \dots 20$$

where  $d_a$  is the density of air in g/ml. Duplicate results did not differ by more than  $\pm 0.0005$  g/ml.

### Experimental Results

The effect of solvent and temperature on the diffusion coefficient was investigated for a series of organic nitro compounds. Polarographic diffusion currents and viscosities were determined in 0.1M LiCl-ethylene glycol and 0.1M



TABLE VII. PYCNOMETER CALIBRATION FACTORS

Temperature, °C	Pycnometer Number <sup>a</sup> and Constant, $F_t$ (ml <sup>-1</sup> )		
	1	2	3
0	0.040728	0.036548	0.36105
20	0.040723	0.036547	0.36170
40	0.040660	0.036536	0.36118
60	0.040562	0.036523	0.36160
80	0.040412	0.036503	
100	0.040211	0.036487	

a. Pycnometer numbers 1 and 2 refer to the 25 ml pycnometers, number 3 refers to the 3 ml pycnometer.





LiCl-glycerol solutions of the nitro compounds for temperatures ranging from 0° to 100°C. Diffusion current constants obtained by polarography are shown in Tables XI - XIX. The polarographic results for 2-nitrobutane in 0.1M LiCl-glycerol, Table XV, are low in comparison with the other results. No explanation for this obviously inconsistent data can be offered. Densities of the solvent systems and the nitro compounds are given in Table VIII. Viscosities of the solvent systems are in Table IX.

Diffusion coefficients, shown in Tables XXI - XXIV, were computed from the Ilkovic Equation (Equation 4) and the Stokes-Einstein Equation (Equation 11);  $D_I$  refers to the diffusion coefficient calculated from the Ilkovic Equation and  $D_{SE}$  refers to the diffusion coefficient calculated from the Stokes-Einstein Equation.



TABLE VIII. VARIATION OF DENSITY WITH TEMPERATURE OF NITRO COMPOUNDS, 0.1M LiCl-ETHYLENE GLYCOL AND 0.1M LiCl-GLYCEROL

Substance	Density, g/ml					
	0°	20°	40°	60°	80°	100°C
Nitroethane	1.068	1.050	1.025			
1-Nitropropane	1.016	1.001	0.979			
2-Nitropropane	1.007	0.990	0.969			
1-Nitrobutane	0.989	0.971	0.953	0.934		
2-Nitrobutane	0.989	0.976	0.956	0.937		
Nitrobenzene	1.220	1.205	1.184	1.164	1.145	1.125
o-Nitrotoluene	1.181	1.164	1.145	1.125	1.106	1.082
2-Nitro-p-xylene	1.140	1.128	1.109	1.092	1.072	1.054
3-Nitro-o-xylene	1.155	1.140	1.121	1.103	1.082	1.067
0.1M LiCl-Ethylene glycol <sup>a</sup>	1.125	1.116	1.103	1.089	1.072	1.056
0.1M LiCl-Glycerol	1.271	1.262	1.253	1.239	1.225	1.212

a. 0.005 percent in gelatin.





TABLE IX. VARIATION OF VISCOSITY WITH TEMPERATURE OF 0.1M  
LiCl-ETHYLENE GLYCOL SOLUTIONS AND 0.1M LiCl-GLYCEROL  
SOLUTIONS

Viscosity, poise				
0.1M LiCl-Ethylene Glycol <sup>a</sup>			0.1M LiCl-Glycerol	
Temp.,		Standard		Standard
°C	<u>Viscosity</u>	<u>Error of</u> <u>the Mean</u>	<u>Viscosity</u>	<u>Error of</u> <u>the Mean</u>
0	0.6200	0.0009 <sub>7</sub>	130.3	0.1
20	0.2233	0.0003	15.44	0.01
40	0.1017	0.0001	3.163	0.001
60	0.05459	0.00008	0.8796	0.0002
80	0.03281	0.00002	0.3385	0.0001
100	0.02151	0.00001	0.1573	0.0001

a. 0.005 percent in gelatin.



### III DISCUSSION

#### General

As stated previously, a change of solvent from aqueous solution can affect the diffusion current in several ways. First, a change in the surface tension of the mercury may cause a change in the capillary constant; and second, a change in viscosity may cause a change in the diffusion coefficient. It can be seen from Tables I and II that the capillary constant over a temperature range of 100°C is relatively constant, i.e. 1.54 to 1.50  $\text{mg}^{2/3} \text{sec}^{-1/2}$  in 0.1M LiCl-ethylene glycol and 1.62 to 1.74  $\text{mg}^{2/3} \text{sec}^{-1/2}$  in 0.1M LiCl-glycerol. The variation observed, ca. 3 percent in 0.1M LiCl-ethylene glycol and ca. 7 percent in 0.1M LiCl-glycerol, is totally accounted for in the diffusion current constant,  $I_d$ . Changes in the diffusion current constant must therefore result from changes in the diffusion coefficient.

If we combine the Ilkovic Equation in the form

$$I_d = 607 n D^{1/2} \dots 21$$

with the Stokes-Einstein expression for the diffusion coefficient, Equation 13, we obtain

$$I_d = 607 n \left[ \sqrt{\frac{k}{a \eta}} \left( \frac{N}{V} \right)^{1/3} \right] \left( \frac{T}{\eta} \right)^{1/2} \dots 22.$$





Equation 22 predicts a linear relation between the diffusion current constant and the temperature-viscosity ratio. Since we are dealing with non-ionic diffusing species the assumption that no solvation occurs in the two solvents employed seems reasonable. Hence we should be able to express the radius of the diffusing species in terms of the molar volume, i.e. Equation 10. The values of the term  $(N/V)^{1/3}$  are listed in Table X. This term is somewhat different for different compounds. The justification for assuming the same value for the number of electrons involved in the reduction process in the two solvents is based on the evidence summarized in the introduction. It follows that the variation in the diffusion current constant must result from a change in the diffusion coefficient since the diffusion coefficient should be directly related to the viscosity of the solvent according to Equation 22.

From the above consideration, a plot of  $I_d$  vs  $(T/\eta)^{1/2}$  should result in a linear relation if the coefficient "a" in Equation 22 is assumed to be constant for a particular small molecule diffusing in a viscous solvent. In other words,



TABLE X. VALUES OF THE TERM  $(N/V)^{1/3}$  FOR VARIOUS NITRO  
COMPOUNDS AT VARIOUS TEMPERATURES

<u>Substance</u>	$(N/V)^{1/3}, \text{ cm x } 10^{-7}$					
	<u>0°</u>	<u>20°</u>	<u>40°</u>	<u>60°</u>	<u>80°</u>	<u>100° C</u>
Nitroethane	2.05	2.03	2.02			
1-Nitropropane	1.90	1.89	1.87			
2-Nitropropane	1.89	1.89	1.87			
1-Nitrobutane	1.80	1.79	1.77	1.76		
2-Nitrobutane	1.80	1.79	1.77	1.76		
Nitrobenzene	1.82	1.81	1.80	1.79	1.78	1.77
o-Nitrotoluene	1.73	1.72	1.71	1.70	1.70	1.68
2-Nitro-p-xylene	1.66	1.65	1.64	1.63	1.62	1.61
3-Nitro-o-xylene	1.66	1.65	1.64	1.63	1.63	1.62





if the above assumptions are applicable, the product  $I_d(\eta/T)^{1/2}$  should be constant for any one solute and the only other variable affecting the diffusion coefficient is the temperature-viscosity ratio. Values of the diffusion current constant,  $I_d$ , along with the temperature-viscosity ratio, are listed in Tables XI to XIX. As can be seen, the diffusion current constant increases by a factor of ca. 6 when going from 0° to 100°C in 0.1M LiCl-ethylene glycol. On the other hand, the diffusion current constant in 0.1M LiCl-glycerol increases by a factor of ca. 35 for the same temperature change because of a much greater relative change of viscosity with temperature. The increase of the temperature-viscosity ratio for an increase in temperature from 0° to 100°C is of the same order of magnitude as the increase in the diffusion current constant, i.e. a factor of ca. 6 in 0.1M LiCl-ethylene glycol and a factor of ca. 34 in 0.1M LiCl-glycerol. A plot of  $I_d$  vs  $(T/\eta)^{1/2}$  for nitrobenzene in 0.1M LiCl-ethylene glycol and in 0.1M LiCl-glycerol, shown in Figure 10, is a typical example of what was observed for the compounds studied. It is noted that the plot is linear even though there is some variation of  $I_d$  with  $(T/\eta)^{1/2}$  for a particular solvent. However, the results for the two solvents are on different straight lines.

Table XX summarizes the values of the product  $I_d(\eta/T)^{1/2}$  from Tables XI - XIX. Table XX illustrates the



TABLE XI. TEMPERATURE-VISCOSITY RATIOS, DIFFUSION CURRENT CONSTANTS AND THEIR PRODUCT, FOR NITROETHANE IN 0.1M LiCl-ETHYLENE GLYCOL AND IN 0.1M LiCl-GLYCEROL

Nitroethane			Diffusion	
Concentration, millimoles/liter	Temp., °C	$(T/\eta)^{1/2}$ , $(^{\circ}\text{K}/\text{poise})^{1/2}$	Current Constant <sup>a</sup>	$I_d (\eta/T)^{1/2}$ <sup>b</sup>
1.13 <sup>c</sup>	0	21.0	1.44	6.85
	20	36.2	2.33	6.43
	40	55.5	3.38	6.08
0.98 <sup>d</sup>	0	1.45	0.0437	3.02
	20	4.36	0.136	3.13
	40	9.95	0.326	3.23

a.  $I_d = i_d / \text{Cm}^{2/3} t^{1/6}$ , microamperes millimolar<sup>-1</sup>mg<sup>-2/3</sup>sec<sup>1/2</sup>.

b.  $\times 10^2$ .

c. 0.1M LiCl-ethylene glycol, 0.005 percent in gelatin.

d. 0.1M LiCl-glycerol.





TABLE XII. TEMPERATURE-VISCOSITY RATIOS, DIFFUSION CURRENT CONSTANTS AND THEIR PRODUCT, FOR 1-NITROPROPANE IN 0.1M LiCl-ETHYLENE GLYCOL AND IN 0.1M LiCl-GLYCEROL

1-Nitropropane			Diffusion	
Concentration, millimoles/liter	Temp., °C	$(T/\eta)^{1/2}$ , $(^{\circ}\text{K}/\text{poise})^{1/2}$	Current Constant <sup>a</sup>	$I_d(\eta/T)^{1/2}$ <sup>b</sup>
0.99 <sup>c</sup>	0	21.0	1.28	6.09
	20	36.2	2.18	6.02
	40	55.5	3.11	5.60
1.01 <sup>d</sup>	0	1.45	0.0436	3.01
	20	4.36	0.134	3.08
	40	9.95	0.322	3.24

a.  $I_d = i_d / C m^{2/3} t^{1/6}$ , microamperes millimolar<sup>-1</sup> mg<sup>-2/3</sup> sec<sup>1/2</sup>.

b.  $\times 10^2$ .

c. 0.1M LiCl-ethylene glycol, 0.005 percent in gelatin.

d. 0.1M LiCl-glycerol.



TABLE XIII. TEMPERATURE-VISCOSITY RATIOS, DIFFUSION CURRENT CONSTANTS AND THEIR PRODUCT, FOR 2-NITROPROPANE IN 0.1M LiCl-ETHYLENE GLYCOL AND IN 0.1M LiCl-GLYCEROL

2-Nitropropane			Diffusion	
Concentration, millimoles/liter	Temp., °C	$(T/\eta)^{1/2}$ , $(^{\circ}\text{K}/\text{poise})^{1/2}$	Current Constant <sup>a</sup>	$I_d(\eta/T)^{1/2}$ <sup>b</sup>
0.91 <sup>c</sup>	0	21.0	1.09	5.12
	20	36.2	1.86	5.13
	40	55.5	2.60	4.68
1.15 <sup>d</sup>	0	1.45	0.0412	2.85
	20	4.36	0.130	2.99
	40	9.95	0.309	3.10

a.  $I_d = i_d / C m^{2/3} t^{1/6}$ , microamperes millimolar<sup>-1</sup> mg<sup>-2/3</sup> sec<sup>1/2</sup>.

b.  $\times 10^2$ .

c. 0.1M LiCl-ethylene glycol, 0.005 percent in gelatin.

d. 0.1M LiCl-glycerol.



TABLE XIV. TEMPERATURE-VISCOSITY RATIOS, DIFFUSION CURRENT CONSTANTS AND THEIR PRODUCT, FOR 1-NITROBUTANE IN 0.1M LiCl-ETHYLENE GLYCOL AND IN 0.1M LiCl-GLYCEROL

1-Nitrobutane			Diffusion	
Concentration, millimoles/liter	Temp., °C	$(T/\eta)^{1/2}$ , $(^{\circ}\text{K}/\text{poise})^{1/2}$	Current Constant <sup>a</sup>	$I_d(\eta/T)^{1/2}$ <sup>b</sup>
1.13 <sup>c</sup>	0	21.0	1.07	5.09
	20	36.2	1.75	4.83
	40	55.5	2.55	4.59
	60	78.1	3.33	4.26
1.05 <sup>d</sup>	0	1.45	0.0345	2.38
	20	4.36	0.111	2.55
	40	9.95	0.282	2.83
	60	19.5	0.541	2.78

a.  $I_d = i_d / C m^{2/3} t^{1/6}$ , microamperes millimolar<sup>-1</sup> mg<sup>-2/3</sup> sec<sup>1/2</sup>.

b.  $\times 10^2$ .

c. 0.1M LiCl-ethylene glycol, 0.005 percent in gelatin.

d. 0.1M LiCl-glycerol.





TABLE XV. TEMPERATURE-VISCOSITY RATIOS, DIFFUSION CURRENT CONSTANTS AND THEIR PRODUCT, FOR 2-NITROBUTANE IN 0.1M LiCl-ETHYLENE GLYCOL AND IN 0.1M LiCl-GLYCEROL

2-Nitrobutane			Diffusion	
Concentration, millimoles/liter	Temp., °C	$(T/\eta)^{1/2}$ , $(^{\circ}\text{K}/\text{poise})^{1/2}$	Current Constant <sup>a</sup>	$I_d(\eta/T)^{1/2}$ <sup>b</sup>
1.02 <sup>c</sup>	0	21.0	1.21	5.76
	20	36.2	1.95	5.38
	40	55.5	2.94	5.29
	60	78.1	4.03	5.16
0.63 <sup>d</sup>	0	1.45	0.0228	1.58
	20	4.36	0.0561	1.29
	40	9.95	0.133	1.34
	60	19.5	0.246	1.26

a.  $I_d = i_d / C m^{2/3} t^{1/6}$ , microamperes millimolar<sup>-1</sup>mg<sup>-2/3</sup>sec<sup>1/2</sup>.

b.  $\times 10^2$ .

c. 0.1M LiCl-ethylene glycol, 0.005 percent in gelatin.

d. 0.1M LiCl-glycerol.



TABLE XVI. TEMPERATURE-VISCOSITY RATIOS, DIFFUSION CURRENT CONSTANTS AND THEIR PRODUCT, FOR NITROBENZENE IN 0.1M LiCl-ETHYLENE GLYCOL AND IN 0.1M LiCl-GLYCEROL

Nitrobenzene			Diffusion	
Concentration, millimoles/liter	Temp., °C	$(T/\eta)^{1/2}$ , $(^{\circ}\text{K}/\text{poise})^{1/2}$	Current Constant <sup>a</sup>	$I_d(\eta/T)^{1/2}$ <sup>b</sup>
1.00 <sup>c</sup>	0	21.0	1.22	5.81
	20	36.2	2.04	5.63
	40	55.5	3.26	5.87
	60	78.1	4.58	5.86
	80	104	5.79	5.59
	100	132	7.18	5.46
1.07 <sup>d</sup>	0	1.45	0.0548	3.79
	20	4.36	0.188	4.32
	40	9.95	0.448	4.50
	60	19.5	0.896	4.61
	80	32.3	1.40	4.34
	100	48.7	2.16	4.33

a.  $I_d = i_d / C m^{2/3} t^{1/6}$ , microamperes millimolar<sup>-1</sup> mg<sup>-2/3</sup> sec<sup>1/2</sup>.

b.  $\times 10^2$ .

c. 0.1M LiCl-ethylene glycol, 0.005 percent in gelatin.

d. 0.1M LiCl-glycerol.





TABLE XVII. TEMPERATURE-VISCOSITY RATIOS, DIFFUSION CURRENT CONSTANTS AND THEIR PRODUCT, FOR o-NITROTOLUENE IN 0.1M LiCl-ETHYLENE GLYCOL AND IN 0.1M LiCl-GLYCEROL

o-Nitrotoluene			Diffusion	
Concentration, millimoles/liter	Temp., °C	$(T/\eta)^{1/2}$ , $(^{\circ}\text{K}/\text{poise})^{1/2}$	Current Constant <sup>a</sup>	$I_d(\eta/T)^{1/2}$ <sup>b</sup>
1.03 <sup>c</sup>	0	21.0	1.11	5.28
	20	36.2	1.95	5.38
	40	55.5	2.92	5.26
	60	78.1	4.10	5.25
	80	104	5.39	5.20
	100	132	6.27	4.77
1.00 <sup>d</sup>	0	1.45	0.0531	3.67
	20	4.36	0.168	3.68
	40	9.95	0.410	4.12
	60	19.5	0.784	4.03
	80	32.3	1.33	4.12
	100	48.7	1.85	3.79

a.  $I_d = i_d / \text{Cm}^{2/3} \text{t}^{1/6}$ , microamperes millimolar<sup>-1</sup>mg<sup>-2/3</sup>sec<sup>1/2</sup>.

b.  $\times 10^2$ .

c. 0.1M LiCl-ethylene glycol, 0.005 percent in gelatin.

d. 0.1M LiCl-glycerol.



TABLE XVIII. TEMPERATURE-VISCOSITY RATIOS, DIFFUSION CURRENT CONSTANTS AND THEIR PRODUCT, FOR 2-NITRO-p-XYLENE IN 0.1M LiCl-ETHYLENE GLYCOL AND IN 0.1M LiCl-GLYCEROL

2-Nitro-p-xylene			Diffusion	
Concentration,	Temp.,	$(T/\eta)^{1/2}$ ,	Current	
<u>millimoles/liter</u>	<u>°C</u>	<u>(°K/poise)<sup>1/2</sup></u>	<u>Constant<sup>a</sup></u>	<u><math>I_d(\eta/T)^{1/2}</math><sup>b</sup></u>
1.06 <sup>c</sup>	0	21.0	1.08	5.14
	20	36.2	1.87	5.16
	40	55.5	2.94	5.29
	60	78.1	4.00	5.12
	80	104	5.10	4.92
	100	132	6.15	4.67
1.00 <sup>d</sup>	0	1.45	0.0506	3.50
	20	4.36	0.152	3.50
	40	9.95	0.393	3.95
	60	19.5	0.733	3.77
	80	32.3	1.24	3.84
	100	48.7	1.80	3.69

a.  $I_d = i_d/Cm^{2/3}t^{1/6}$ , microamperes millimolar<sup>-1</sup>mg<sup>-2/3</sup>sec<sup>1/2</sup>.

b.  $\times 10^2$ .

c. 0.1M LiCl-ethylene glycol, 0.005 percent in gelatin.

d. 0.1M LiCl-glycerol.



TABLE XIX. TEMPERATURE-VISCOSITY RATIOS, DIFFUSION CURRENT CONSTANTS AND THEIR PRODUCT, FOR 3-NITRO-o-XYLENE IN 0.1M LiCl-ETHYLENE GLYCOL AND IN 0.1M LiCl-GLYCEROL

3-Nitro-o-xylene			Diffusion	
Concentration, millimoles/liter	Temp., °C	$(T/\eta)^{1/2}$ , $(^{\circ}\text{K}/\text{poise})^{1/2}$	Current Constant <sup>a</sup>	$I_d(\eta/T)^{1/2}$ <sup>b</sup>
1.02 <sup>c</sup>	0	21.0	1.07	5.09
	20	36.2	1.81	5.00
	40	55.5	2.83	4.09
	60	78.1	4.08	5.22
	80	104	5.12	4.94
	100	132	6.05	4.60
1.02 <sup>d</sup>	0	1.45	0.0603	4.17
	20	4.36	0.188	4.32
	40	9.95	0.470	4.72
	60	19.5	0.872	4.48
	80	32.3	1.43	4.43
	100	48.7	2.04	4.18

a.  $I_d = i_d/\text{Cm}^{2/3}t^{1/6}$ , microamperes millimolar<sup>-1</sup>mg<sup>-2/3</sup>sec<sup>1/2</sup>.

b.  $\times 10^2$ .

c. 0.1M LiCl-ethylene glycol, 0.005 percent in gelatin.

d. 0.1M LiCl-glycerol.





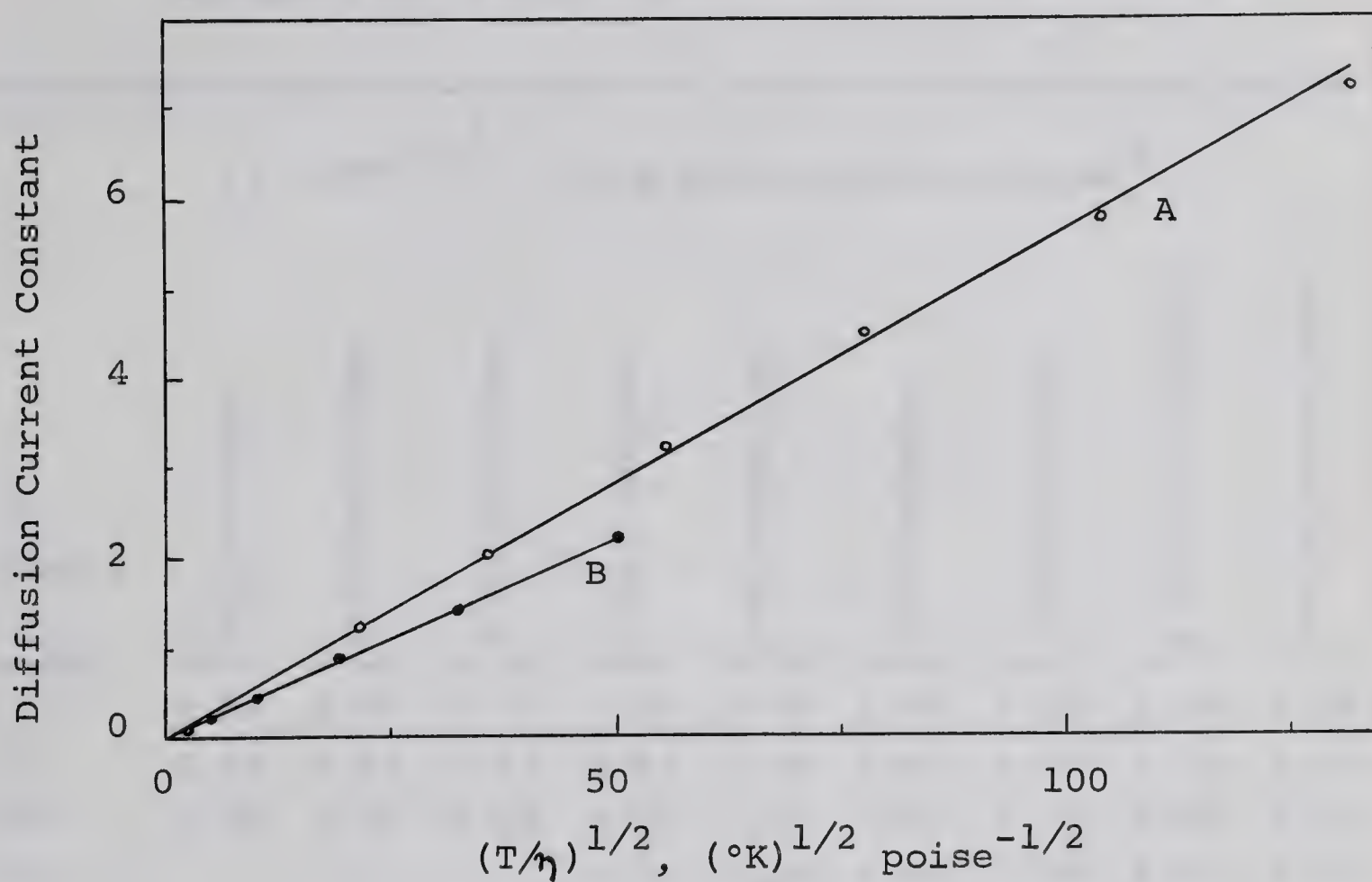


Figure 10. An example of the variation of the diffusion current constant with the temperature-viscosity ratio, for nitrobenzene in 0.1M LiCl-ethylene glycol (A) and in 0.1M LiCl-glycerol (B). The diffusion current constant is  $i_d/Cm^{2/3}t^{1/6}$ , microamperes millimolar<sup>-1</sup> mg<sup>-2/3</sup> sec<sup>1/2</sup>.



TABLE XX. VALUES OF THE PRODUCT OF THE DIFFUSION CURRENT  
CONSTANT AND THE VISCOSITY-TEMPERATURE RATIO

$I_d (\eta/T)^{1/2^a}, \quad 0.1M \text{ LiCl-Ethylene Glycol}^b$									
Temp., °C	Nitroethane	1-Nitropropane	2-Nitropropane	1-Nitrobutane	2-Nitrobutane	Nitrobenzene	o-Nitrotoluene	2-Nitro-p-xylene	3-Nitro-o-xylene
0	6.85	6.09	5.12	5.09	5.76	5.81	5.28	5.14	5.09
20	6.43	6.02	5.13	4.83	5.38	5.63	5.38	5.16	5.00
40	6.08	5.60	4.68	4.59	5.29	5.87	5.26	5.29	5.09
60				4.26	5.16	5.86	5.25	5.12	5.22
80						5.59	5.20	4.92	4.94
100						5.46	4.77	4.67	4.60
$I_d (\eta/T)^{1/2}, \quad 0.1M \text{ LiCl-Glycerol}$									
0	3.02	3.01	2.85	2.38	1.58	3.79	3.67	3.50	4.17
20	3.13	3.08	2.99	2.55	1.29	4.32	3.68	3.50	4.32
40	3.23	3.24	3.10	2.83	1.34	4.50	4.12	3.95	4.72
60				2.78	1.26	4.61	4.03	3.77	4.48
80						4.34	4.12	3.84	4.43
100						4.33	3.79	3.69	4.18

a. (microamperes millimolar<sup>-1</sup>mg<sup>-2/3</sup>sec<sup>1/2</sup>poise<sup>1/2</sup>°K<sup>-1/2</sup>)x10<sup>2</sup>.

b. 0.005 percent in gelatin.





relative constancy of the product for any one compound in one solvent at a series of temperatures. It is also clear that the product varies from compound to compound. It was hoped that any difference in the product for different solutes could be totally accounted for by the difference in the value of  $(N/V)^{1/3}$  of Equation 22. In general as  $(N/V)^{1/3}$  decreases so does the product  $I_d (\eta/T)^{1/2}$ , but the changes in  $(N/V)^{1/3}$  account only for a minor part of the change in  $I_d (\eta/T)^{1/2}$ . For instance, in 0.1M LiCl-ethylene glycol at 0°C the value of  $(N/V)^{1/3}$  changes from  $2.05 \times 10^7$  for nitroethane to  $1.80 \times 10^7$  for 1-nitrobutane, i.e. a change of ca. 3.5 percent in the term  $(N/V)^{1/3}$  whereas  $I_d (\eta/T)^{1/2}$  changes ca. 25 percent for these two substances at the same temperature. Similarly, in 0.1M LiCl-glycerol at 0°C the product  $I_d (\eta/T)^{1/2}$  changes ca. 20 percent for these two substances at the same temperature.

As has been pointed out in the introduction it was hoped that one could measure diffusion coefficients by polarographic means and by correlation of these measurements with the more simply measured property of viscosity one could obtain diffusion coefficients for a wide variety of solvents. It is therefore of interest to compare diffusion coefficients obtained from the Ilkovic Equation (Equation 4) with those calculated from the Stokes-Einstein Equation (Equation 11).



Table XXI summarizes the values of the diffusion coefficient calculated from these two equations for the several nitro compounds in 0.1M LiCl-ethylene glycol at temperatures 0° to 100°C. If the two sections of the table are compared it is clear that the diffusion coefficient calculated from polarographic measurements is larger than that calculated from viscosity data, i.e.  $D_I > D_{SE}$ . This is not unexpected if we consider Equation 11. As stated previously, Equation 11 is applicable when the size of the diffusing species is slightly larger than or approximately equal to the size of the solvent molecules. When one applies Equation 11 to the situation of a diffusing species much larger than the solvent molecules the factor  $2\pi$  in Equation 11 is replaced by a larger factor, i.e.  $4\pi$ . Hence, one would expect that the factor  $2\pi$  of Equation 11 should be replaced by a smaller factor when one applies Equation 11 to the situation of a diffusing species smaller than the solvent molecules (32). This is consistent with the data of Table XXI in which diffusion coefficients calculated from the Ilkovic Equation are larger than those calculated from Equation 11.

The results of Table XXI have been compared with the small amount of information available in the literature for organic nitro compounds in ethylene glycol-based solutions. The results in Table XXII have been calculated from the





TABLE XXI. DIFFUSION COEFFICIENTS OF ORGANIC NITRO COMPOUNDS  
IN 0.1M LiCl-ETHYLENE GLYCOL<sup>a</sup> CALCUATED FROM THE ILKOVIC  
EQUATION AND FROM THE STOKES-EINSTEIN EQUATION<sup>c</sup>

Diffusion Coefficients <sup>b</sup> from the Ilkovic Equation									
Temp., °C	Nitroethane	1-Nitropropane	2-Nitropropane	1-Nitrobutane	2-Nitrobutane	Nitrobenzene	o-Nitrotoluene	2-Nitro-p-xylene	3-Nitro-o-xylene
0	3.37	2.85	2.18	1.93	2.45	2.59	2.18	1.95	2.00
20	9.77	8.15	6.08	5.09	6.45	7.20	6.35	5.97	5.64
40	19.6	16.8	13.2	11.0	14.7	18.3	14.8	13.8	13.7
60				19.0	28.1	35.8	30.6	27.5	28.5
80						53.8	49.8	46.6	45.6
100						86.9	70.3	65.1	62.3

Diffusion Coefficient <sup>b</sup> from the Stokes-Einstein Equation <sup>c</sup>									
0	1.98	1.84	1.83	1.74	1.73	1.75	1.67	1.60	1.61
20	5.87	5.45	5.43	5.14	5.14	5.20	4.96	4.75	4.77
40	13.7	12.7	12.6	12.0	12.0	12.1	11.6	11.1	11.1
60				23.6	23.6	23.9	22.8	21.9	21.9
80						41.9	39.9	38.3	38.4
100						67.2	64.0	61.4	61.7

a. 0.005 percent in gelatin.

b.  $\text{cm}^2\text{sec}^{-1} \times 10^7$ .

c. Equation 11.





TABLE XXII. DIFFUSION COEFFICIENTS OF NITROETHANE, 1- AND 2-NITROPROPANE IN 0.3M LiCl-ETHYLENE GLYCOL AND IN 0.1M LiCl-ETHYLENE GLYCOL

Substance	Diffusion Coefficient <sup>a</sup>			
	0.3M LiCl-Ethylene Glycol <sup>b</sup>		0.1M LiCl-Ethylene Glycol <sup>c</sup>	
	$\underline{D_I^d}$	$\underline{D_{SE}^e}$	$\underline{D_I}$	$\underline{D_{SE}}$
Nitroethane	9.8	5.8	11.4	7.6
1-Nitropropane	8.3	5.3	9.7	6.9
2-Nitropropane	7.5	5.3	7.4	6.9

a.  $\text{cm}^2\text{sec}^{-1} \times 10^7$ , temperature 25°C.

b. Calculated from the data of Radin and DeVries (38).

c. 0.005 percent in gelatin, present work.

d. Diffusion coefficient from the Ilkovic Equation.

e. Diffusion coefficient from the Stokes-Einstein Equation, Equation 11.



polarographic data of Radin and DeVries (38) and the polarographic and viscosity data of the author. For calculations involving Equation 11 the viscosity of the 0.3M LiCl-ethylene glycol solution used by Radin and DeVries was estimated from viscosity data of pure ethylene glycol (6) and the viscosity data presented in Table IX. According to Bingham (4) the fluidity,  $1/\eta$ , of a dilute solution varies directly with the concentration of added electrolyte. For aqueous solutions of lithium chloride, Bingham reports a decrease in the fluidity with added electrolyte, e.g. at 25°C the fluidity varies linearly for concentrations of 0 to 1M LiCl from 105 to 98 poise<sup>-1</sup>. On the basis of this linearity it is estimated that the viscosity of the 0.3M LiCl-ethylene glycol solution is 0.243 poise. Values of the diffusion coefficient at 25°C in 0.1M LiCl-ethylene glycol were obtained by interpolation of the diffusion coefficient-temperature graphs obtained from the data in Table XXI. It is clear from Table XXII that the data of Radin and DeVries generally substantiates the conclusion of the preceeding paragraph that diffusion coefficients calculated from the Ilkovic Equation are greater than those calculated from Equation 11 for the solvent ethylene glycol.

On the basis of what was observed for the ethylene glycol-based solutions we might predict that the same trend should occur for the same species diffusing in 0.1M LiCl-





glycerol, i.e.  $D_I > D_{SE}$ . Table XXIII summarizes the values of the diffusion coefficient calculated from the Ilkovic Equation and from Equation 11 for the same nitro compounds in 0.1M LiCl-glycerol at temperatures 0° to 100°C. From a comparison of the two sections of the table it is clear that the diffusion coefficient calculated from viscosity data is larger than that calculated from polarographic measurements, i.e.  $D_{SE} > D_I$ . This is in direct contradiction to what was expected. Again the results have been compared with the limited data available for organic nitro compounds in glycerol-based solutions. The results in Table XXIV have been calculated from the polarographic data of Radin and DeVries (38) for some nitroparaffins in 0.3M LiCl-glycerol. For calculations involving Equation 11 the viscosity of 0.3M LiCl-glycerol was estimated in the same manner as for the 0.3M LiCl-ethylene glycol solutions. The viscosity of the 0.3M LiCl-glycerol was estimated to be 13.7 poise. As with the diffusion coefficients in 0.1M LiCl-ethylene glycol, the diffusion coefficients at 25°C in 0.1M LiCl-glycerol were obtained by interpolation of the diffusion coefficient-temperature graphs obtained from the data in Table XXIII. It is apparent from Table XXIV that the results obtained from the data of Radin and DeVries confirm the data of Table XXIII that the diffusion coefficients calculated from Equation 11 are greater than those calculated from the Ilkovic



TABLE XXIII. DIFFUSION COEFFICIENTS OF ORGANIC NITRO COMPOUNDS  
IN 0.1M LiCl-GLYCEROL CALCULATED FROM THE ILKOVIC EQUATION AND  
THE STOKES-EINSTEIN EQUATION<sup>b</sup>

Diffusion Coefficient <sup>a</sup> from the Ilkovic Equation									
Temp., °C	Nitroethane	1-Nitropropane	2-Nitropropane	1-Nitrobutane	2-Nitrobutane	Nitrobenzene	o-Nitrotoluene	2-Nitro-p-xylene	3-Nitro-o-xylene
0	0.0033	0.0032	0.0029	0.0021	0.0009	0.0054	0.0049	0.0044	0.0063
20	0.0313	0.0309	0.0291	0.0206	0.0054	0.0605	0.0482	0.0424	0.0603
40	0.184	0.178	0.162	0.138	0.0310	0.342	0.296	0.266	0.379
60				0.492	0.105	1.38	1.07	0.910	1.31
80						3.35	2.84	2.65	3.54
100						8.07	5.75	5.53	7.11

Diffusion Coefficient <sup>a</sup> from the Stokes-Einstein Equation <sup>b</sup>									
0	0.0094	0.0087	0.0087	0.0083	0.0083	0.0083	0.0080	0.0076	0.0076
20	0.0849	0.0789	0.0786	0.0744	0.0745	0.0753	0.0718	0.0688	0.0690
40	0.439	0.408	0.406	0.385	0.385	0.390	0.372	0.356	0.358
60				1.46	1.46	1.48	1.42	1.36	1.36
80						4.07	3.88	3.72	3.73
100						9.19	8.75	8.40	8.44

a.  $\text{cm}^2 \text{sec}^{-1} \times 10^7$ .

b. Equation 11.





TABLE XXIV. DIFFUSION COEFFICIENTS OF NITROETHANE, 1- AND 2-NITROPROPANE IN 0.3M LiCl-GLYCEROL AND IN 0.1M LiCl-GLYCEROL

Substance	Diffusion Coefficient <sup>a</sup>			
	0.3M LiCl-Glycerol <sup>b</sup>		0.1M LiCl-Glycerol <sup>c</sup>	
	$\underline{D_I^d}$	$\underline{D_{SE}^e}$	$\underline{D_I}$	$\underline{D_{SE}}$
Nitroethane	0.07	0.10	0.050	0.13
1-Nitropropane	0.07	0.095	0.047	0.12
2-Nitropropane	0.02	0.095	0.046	0.12

a.  $\text{cm}^2 \text{sec}^{-1} \times 10^7$ , temperature 25°C.

b. Calculated from the data of Radin and DeVries (38).

c. Present work.

d. Diffusion coefficient from the Ilkovic Equation.

e. Diffusion coefficient from the Stokes-Einstein Equation, Equation 11.





Equation for the glycerol-based solutions.

### Correction to the Stokes-Einstein Equation

It has been stated by Harris and Habgood (17) that a linear relation exists between  $\log T/\eta$  and  $1/T$  for a variety of solvents, including ethylene glycol and glycerol. However, a plot of this function, Figure 11, from the data in Table IX, displays non-linearity for both 0.1M LiCl-ethylene glycol and 0.1M LiCl-glycerol over the temperature range 0° to 100°C. This non-linearity is readily accounted for by considering the transition theory of Ewell and Eyring (10). Their concern is with associated liquids such as hydrolytic compounds with viscosities and temperature coefficients of viscosity much higher than for analogous nonassociated substances. They attribute the high viscosity observed for associated liquids to the fact that in addition to the normal work required to make a hole, i.e. a vacancy for the diffusing species to enter, the breaking of hydrogen bonds which attach the molecule to surrounding molecules is necessary, before the activated state for flow can be attained. With increasing temperature there is a decreasing number of hydrogen bonds to be broken. Hence, with an increase in temperature there is a decrease in the activation energy for viscous flow. This inconstancy of the activation energy with temper-



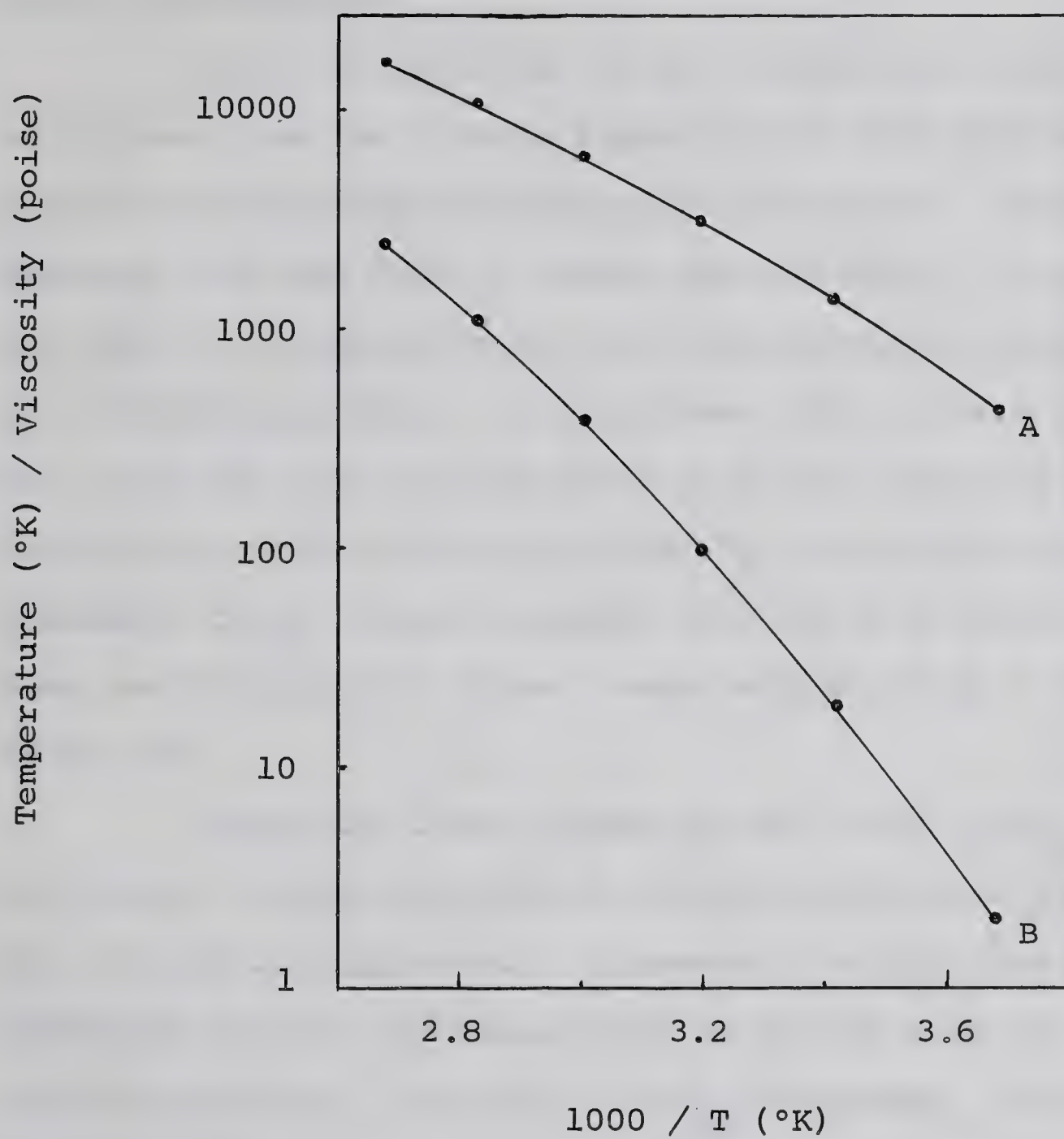


Figure 11. Viscosity-temperature relations for 0.1M LiCl-ethylene glycol (A) and 0.1M LiCl-glycerol (B).





ature accounts for the non-linearity of the  $\log T/\eta$  (or  $\log D$ ) vs  $1/T$  plots.

Plots of  $\log D$  vs  $1/T$  for diffusion coefficients calculated from the Ilkovic Equation and from Equation 11 display the same non-linearity described above. Figure 12, obtained from the data in Tables XXI and XXIII, illustrates the case of nitrobenzene in 0.1M LiCl-ethylene glycol and in 0.1M LiCl-glycerol. It is evident that Curve B would lie along the same line as Curve A if the diffusion coefficients for Curve B were multiplied by a factor of about 1.4. Similarly Curve C would coincide with Curve D if the diffusion coefficients for Curve C were multiplied by a factor of about 0.8.

Table XXV lists values of the ratio  $D_I/D_{SE}$  for the organic nitro compounds in 0.1M LiCl-ethylene glycol and in 0.1M LiCl-glycerol. In general, as the size of the diffusing species increases relative to the size of the solvent molecules, the ratio  $D_I/D_{SE}$  decreases. For instance, in 0.1M LiCl-ethylene glycol at 0°C the ratio  $D_I/D_{SE}$  is greater than one and decreases from a value of 1.70 for nitroethane to a value of 1.11 for 1-nitrobutane and from 1.48 for nitrobenzene to 1.23 for the nitroxylenes. The data for the glycerol system is less consistent but at 0°C the ratio  $D_I/D_{SE}$  is less than one and decreases in general from a value of 0.35 for nitroethane to a value of 0.25 for 1-nitro-



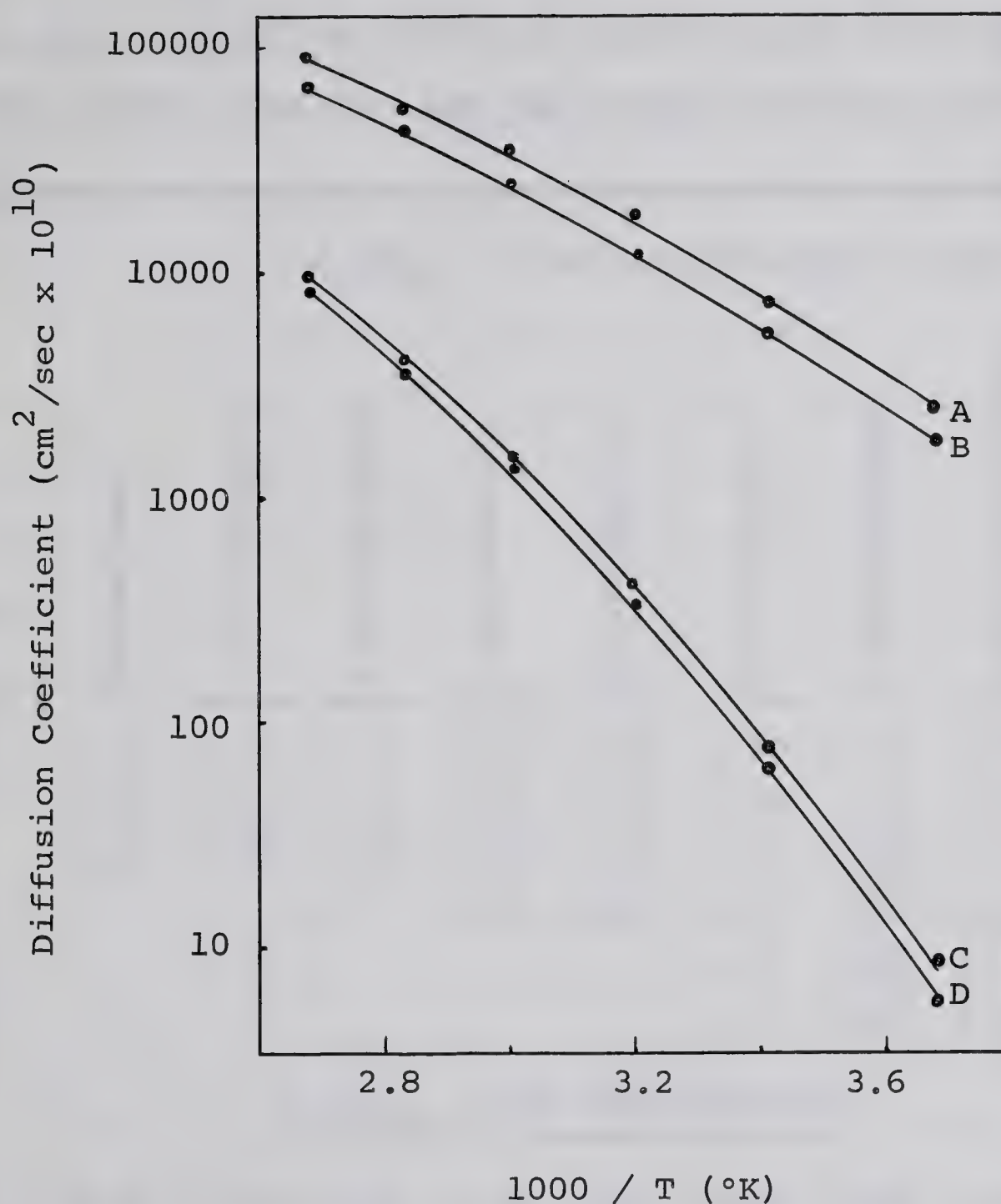


Figure 12. Diffusion coefficients-temperature relations for nitrobenzene in 0.1M LiCl-ethylene glycol (A,B) and in 0.1M LiCl-glycerol (C,D). B,C: diffusion coefficients from Equation 11. A,D: diffusion coefficients from the Ilkovic Equation.





TABLE XXV. RATIO<sup>a</sup> OF DIFFUSION COEFFICIENTS CALCULATED FROM THE ILKOVIC EQUATION AND THE STOKES-EINSTEIN EQUATION<sup>b</sup>

$D_I/D_{SE}$ , 0.1M LiCl-Ethylene Glycol <sup>c</sup>									
Temp., °C	Nitroethane	1-Nitropropane	2-Nitropropane	1-Nitrobutane	2-Nitrobutane	Nitrobenzene	O-Nitrotoluene	2-Nitro-p-xylene	3-Nitro-o-xylene
0	1.70	1.55	1.19	1.11	1.42	1.48	1.31	1.22	1.24
20	1.66	1.50	1.12	0.99	1.25	1.38	1.28	1.26	1.18
40	1.43	1.32	1.05	0.92	1.23	1.51	1.28	1.24	1.23
60				0.81	1.19	1.50	1.34	1.26	1.30
80						1.28	1.25	1.22	1.19
100						1.29	1.10	1.06	1.01
$D_I/D_{SE}$ , 0.1M LiCl-Glycerol									
0	0.35	0.37	0.33	0.25	0.11	0.65	0.61	0.58	0.83
20	0.369	0.392	0.370	0.277	0.072	0.803	0.617	0.616	0.874
40	0.419	0.436	0.399	0.358	0.081	0.877	0.796	0.747	1.06
60				0.370	0.072	0.932	0.754	0.669	0.963
80						0.823	0.732	0.712	0.949
100						0.878	0.657	0.658	0.842

- a.  $D_I/D_{SE}$ ;  $D_I$ , diffusion coefficient calculated from the Ilkovic Equation,  $D_{SE}$ , diffusion coefficient calculated from the Stokes-Einstein Equation.
- b. Equation 11.
- c. 0.005 percent in gelatin.





butane, but without a consistent trend for the aromatic nitro compounds.

It was initially assumed that diffusion coefficients from polarographic measurements and the Ilkovic Equation were correct. With this assumption, diffusion coefficients calculated from Equation 11 were corrected to give the assumed correct value. The value of the coefficient "a" of Equation 13 necessary to give the assumed correct value of the diffusion coefficient can be obtained from the relation

$$a = \frac{2}{D_I/D_{SE}} \quad \dots 23$$

Table XXVI lists values of the coefficient "a" for each of the nitro compounds in 0.1M LiCl-ethylene glycol and in 0.1M LiCl-glycerol. From Table XXVI it would appear that there is a general increase in the coefficient "a" as the size of the diffusing species increases. For instance, in 0.1M LiCl-ethylene glycol at 0°C the value of "a" increases from 1.18 for nitroethane to about 1.6 for the nitrobutanes and from 1.35 for nitrobenzene to 1.62 for the nitroxylenes. Possibly this same trend is revealed in 0.1M LiCl-glycerol at 0°C with the value of "a" increasing in general from 5.77 for nitroethane to 8.04 for 1-nitrobutane, but without a consistent trend for the aromatic nitro compounds. A trend of this sort would be predicted by the theory from which



TABLE XXVI. VALUES OF THE COEFFICIENT "a" FOR NITROPARAFFINS  
AND FOR NITROBENZENES IN 0.1M LiCl-ETHYLENE GLYCOL AND IN  
0.1M LiCl-GLYCEROL

Value of the Coefficient "a", 0.1M LiCl-Ethylene Glycol <sup>a</sup>									
Temp., °C	Nitroethane	1-Nitropropane	2-Nitropropane	1-Nitrobutane	2-Nitrobutane	Nitrobenzene	o-Nitrotoluene	2-Nitro-p-xylene	3-Nitro-o-xylene
0	1.18	1.42	1.68	1.80	1.41	1.35	1.53	1.64	1.61
20	1.20	1.34	1.79	2.02	1.59	1.44	1.52	1.59	1.69
40	1.40	1.51	1.91	2.18	1.63	1.32	1.57	1.61	1.62
60				2.48	1.67	1.34	1.49	1.59	1.54
80						1.56	1.60	1.64	1.68
100						1.55	1.82	1.89	1.98
Value of the Coefficient "a", 0.1M LiCl-Glycerol									
0	5.77	5.41	6.01	8.04	(18.8)	3.10	3.28	3.48	2.42
20	5.43	5.11	5.40	7.22	(27.6)	2.48	2.98	3.25	2.29
40	4.77	4.58	5.01	5.80	(24.8)	2.28	2.51	2.68	1.89
60				5.89	(27.8)	2.15	2.65	2.99	2.08
80						2.44	2.73	2.81	2.11
100						2.88	3.04	3.04	2.37

a. 0.005 percent in gelatin







Equation 13 was derived, i.e. as the size of the diffusing species increases, relative to the size of the solvent molecules, the coefficient "a" should also increase.

Although there appears to be considerable scatter in the value of the coefficient "a" for a particular compound over the temperature range studied, no single trend with temperature is evident from the data in Table XXVI. It is noted in general that the data for the aromatic nitro compounds studied show less scatter than the nitroparaffins. For example, in 0.1M LiCl-ethylene glycol, the coefficient "a" for the nitroparaffins shows a variation of about 15 percent for the temperature range 0° to 40°C. On the other hand, the variation in the coefficient "a" for the aromatic nitro compounds is only about 5 percent for the same temperature range.

In summary it was originally hoped that diffusion coefficients could be obtained from a simply determined property such as viscosity through the Stokes-Einstein Equation. At best it is felt that the diffusion coefficients obtained by the method outlined are valid within only an order of magnitude of the true value. The results in 0.1M LiCl-ethylene glycol generally follow the pattern predicted by existing theory whereas the results in 0.1M LiCl-glycerol are inconsistent with what was expected. On the basis of the data obtained no explanation can be offered for the behaviour



observed in 0.1M LiCl-glycerol. The author now has some doubt as to the validity of the Ilkovic Equation when it is applied to highly viscous solvents such as glycerol. For instance, one observation which requires explanation is that at the same viscosity, in the two different solvents, equal or nearly equal diffusion currents should be obtained. Any slight variation in the diffusion current could then be attributed to a slightly different value for the diffusion coefficient due to the relative size of the diffusing species to the solvent molecules, i.e. the coefficient "a" of Equation 13. It would be interesting to see if the same trend is noticed with another series of organic compounds in the two solvents to either confirm or deny the results obtained from this study. It is suggested by the author that a comparison of diffusion coefficients measured by one of the classical techniques (see Introduction) with those obtained from polarographic measurements be carried out. A study of this kind could possibly provide some insight into the validity of the use of the Ilkovic Equation for determining diffusion coefficients in highly viscous solvents.





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